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[Jour. Indian Chem. Soc., Vol. 34, No. 3, 1957]

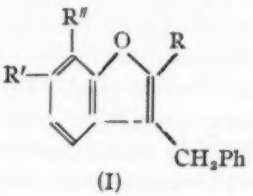
EXPERIMENTS ON THE SYNTHESES OF FURANO COMPOUNDS. PART XI. CYCLODEHYDRATION OF 2-ACYL-3-BENZYLCOUMARONES

By J. N. Chatterjea and S. K. Roy *

2-Acyl-3-benzylcoumarones have been prepared and their cyclodehydration to β-brazans studied.

In this communication, the synthesis of β-brazans by aromatic cyclodehydration of 2-acyl-3-benzylcoumarones, as described in an earlier paper (this *Journal*, 1953, **30**, 1), has been re-examined and extended to a few more cases with a view to studying the scope and limitations of the method. The method appears to be of general application provided that the 2-acylcoumarones are readily synthetically available, and in difficult cases, the Kipping cyclisation of the related 3-benzylcoumarone-2-carboxylic acid affords the alternative solution.

3-Benzylcoumarones, which afford the 2-acylcoumarones by the Hoesch or the Gattermann synthesis, are best prepared by the decarboxylation of the corresponding 2-carboxylic acids. For instance, 6-methoxy-3-benzylcoumarone-2-carboxylic acid (I: R=COOH; R′=OMe ; R″=H), prepared by Bentley and Robinson (*J. Chem. Soc.*, 1950, 1355), gave on decarboxylation with the aid of copper-bronze, 6-methoxy-3-benzylcoumarone which furnished 2-formyl derivative on the Gattermann reaction. The



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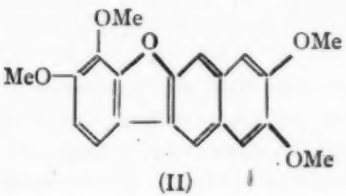

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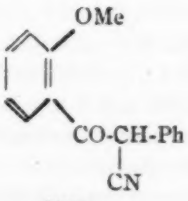

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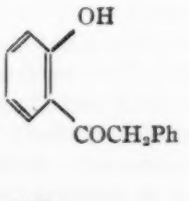

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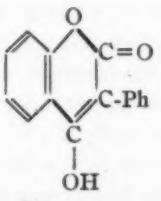

(V)

orientation of this aldehyde was established by its preparation from the corresponding acid, mentioned above, by the Stevens-McFadeyn method (*J. Chem. Soc.*, 1936, 584)

* In part.

involving the decomposition of the sulphonhydrazide (I : R = CONHNHSO$_2$Ph; R′ = OMe; R″ = H) prepared *via* the ester and the hydrazide in the usual manner. On cyclisation with polyphosphoric acid, the aldehyde afforded 3-methoxy-β-brazan in rather a poor yield. It may be noted, however, that the isolation of 3-methoxy-6-hydroxy-β-brazan in substance from the coumarilic acid also proved very difficult (cf. Bentley and Robinson, *loc. cit.*). This has been achieved albeit in unsatisfactory yield, by the cyclisation of the related acid chloride in cold benzene and identified by oxidation to 3-methoxy-β-brazanquinone, synthesised earlier (this *Journal*, 1954, **31**, 101).

3-(3′ : 4′-Dimethoxybenzyl)-6 : 7-dimethoxycoumarone has been prepared from 2-hydroxy-3 : 4-dimethoxyphenyl-(3′ : 4′-dimethoxybenzyl)-ketone in the usual manner. The latter was prepared by the interaction of homoveratroyl chloride with pyrogalloi trimethyl ether in dry ether with the aid of aluminium chloride. This coumarone was successfully converted into the 2-formyl derivative which gave 3 : 4 : 8 : 9-tetramethoxy-β-brazan (II, a possible derivative of haematoxylin) in quantitative yield on cyclodehydration with phosphoric acid.

Our experience with the simplest case, however, has been very unusual. 3-Benzylcoumarone (Chatterjea, this *Journal*, 1955, **32**, 265) has now been prepared from the keto-nitrile (III), obtained by the condensation of *o*-methoxybenzoic ester and phenylacetonitrile. On treatment with boiling hydrobromic acid in acetic acid, this nitrile furnished a mixture of *o*-hydroxyphenylbenzyl ketone (IV) and 3-phenyl-4-hydroxycoumarin (V), separable by steam-distillation or by taking advantage of the latter's solubility in alkali carbonate. The former was converted into 3-benzylcoumarone-2-carboxylic acid and thence by decarboxylation (copper-quinoline) to 3-benzylcoumarone. As reported earlier (Chatterjea, *loc. cit.*), the Gattermann reaction failed entirely with this coumarone **; a *trace* of the aldehyde was obtained on employing the modified reaction (*J. Chem. Soc.*, 1938, 1830; 1939, 132). Alternatively, attempts were made to prepare this aldehyde from the corresponding 2-carboxylic acid. The Rosenmund reaction having yielded a very impure product, recourse was taken to apply the Stevens-McFadeyn procedure as before. Accordingly, the acid was esterified with diazomethane or methanolic sulphuric acid, but the corresponding hydrazide could never be obtained on treating the ester with hydrazine hydrate. The sole product (m. p. 196°), obtained in excellent yield, contained a high percentage of nitrogen, analysing for $C_{16}H_{16}O_2N_4$. This compound behaved as a hydrazide in as much as it reduced Fehling's solution and afforded the original acid on alkaline hydrolysis. It is difficult at this stage to suggest the correct constitution of this extraordinary compound ; a sulphonhydrazide, derived from it, also did not analyse correctly, and failed to provide any aldehyde by decomposition in ethyleneglycol under various conditions. Further work is necessary to elucidate the nature of this abnormal compound. A more encouraging result was obtained by reducing the *N*-methylanilide of the acid with lithium aluminium hydride and hydrolysing the product with acid (cf. Friedman, Abstracts, 116th National Meeting, 5M, 1949; Weygand *et al.*, *Angew Chem.*, 1953, **65**, 525). The aldehyde was obtained in rather

** Formylations of this coumarone and allied compounds with dimethylformamide have been more fruitful. The results will be communicated shortly.

an impure condition which gave a small quantity of β-brazan on cyclodehydration with hydrobromic acid in acetic acid.

2-Acetyl-3-benzylcoumarone was prepared in impure condition from the acid chloride (I : R=COCl ; R′=R″=H) and magnesium malonic ester (cf. Walker and Hauser, *J. Amer. Chem. Soc.*, 1946, **68**, 1386). Attempts to cyclise this ketone so as to obtain 6-methyl-β-brazan have been so far abortive.

Cyclisation of 3-benzylcoumarone-2-carboxylic acid by way of the acid chloride was extremely facile and the product 6-hydroxy-β-brazan was obtained in excellent yield. This compound was converted into β-brazan or the related quinone by reduction or oxidation.

EXPERIMENTAL *

6-Methoxy-3-benzylcoumarone.—6-Methoxy-3-benzylcoumarilic acid (Bentley and Robinson, *loc. cit.*) was heated with a trace of copper-bronze in a metal bath at 220° till the evolution of carbon dioxide was substantially complete, and then distilled in vacuum. The colorless product (yield 50%) solidified immediately and obtained in prisms, m. p. 54° from methanol. The compound gave yellow coloration with sulphuric acid. (Found : C, 81.1 ; H, 5.6. $C_{16}H_{14}O_2$ requires C, 80.7 ; H, 5.9%).

6-Methoxy-2-formyl-3-benzylcoumarone : *Method (a).*—The foregoing coumarone (1.5 g.) in dry ether (40 c.c.) containing $ZnCl_2$ (1 g.) and HCN (4 c.c.) was saturated with anhydrous HCl gas at 0°. The colour of the mixture turned from brown to reddish brown and finally again brown. The crystalline aldimine hydrochloride was collected next day, washed with dry ether, decomposed with water (50 c.c.) and warmed on the water-bath. The crystalline product was filtered, crystallised from alcohol and the *aldehyde* was obtained in colorless needles, m. p. 107°, developing a green colour with H_2SO_4. (Found : C, 77.0 ; H, 5.6. $C_{17}H_{14}O_3$ requires C, 76.7 ; H, 5.3%).

The 2 : 4-*dinitrophenylhydrazone* crystallised from acetic acid in maroon plates, m. p. 213°. (Found : N, 13.0. $C_{23}H_{18}O_6N_4$ requires N, 12.6%).

Method (b).—6-Methoxy-3-benzylcoumarilic acid (3.0 g.) was esterified by boiling with methanolic H_2SO_4 (30 c.c, 8%) for 6 hours. Isolated as usual, the ester (3.0 g.) had no tendency to crystallise. This was then boiled with a mixture of alcohol (15 c.c.) and hydrazine hydrate (10 c.c., 60%, commercial) for 6 hours on the water-bath and then poured into water. The hydrazide (I : R=CONHNH$_2$; R′=OMe ; R″=H) which solidified gradually was collected after 48 hours and obtained in colorless needles (2.2 g.), m. p. 144-48° from alcohol. (Found : N, 9.9. $C_{17}H_{16}O_2N_2$ requires N, 9.5%). A solution of the hydrazide (2.0 g.) in dry pyridine (12 c.c.) was treated at 0° with benzylsulphonyl chloride (1.2 g.), left in the refrigerator for 4 hours and then poured into iced HCl, affording the *sulphonhydrazide* (I : R=CONHNHSO$_2$Ph ; R′=OMe ; R″=H) (2.5 g.) which was collected after washing with cold alcohol. The compound was obtained in colorless prisms, m. p. 254-55° (decomp.) from a large volume of alcohol. (Found : N, 6.9. $C_{23}H_{20}O_5N_2S$ requires N, 6.4%). A suspension of the sulphonhydrazide (0.6 g.) in ethyleneglycol (15 c.c.) at 160° was treated with anhydrous sodium carbonate (0.5 g.). The vigorous reaction that ensued was quenched after 80 seconds

* All m. p's are uncorrected.

by pouring into water. The aldehyde was isolated with ether and obtained in colorless needles (0.15 g.), m.p. and mixed m. p. 107°.

3-Methoxy-β-brazan.—The above aldehyde (1.0 g.) was heated with polyphosphoric acid (10 c.c.) at 100° for 2 hours. The colour of the mixture turned blue from green. After pouring into water, the precipitated compound was collected and purified by several crystallisations from alcohol. The pure product (m.p. 205°) was obtained in a poor yield (Kostanecki and Lampe *Ber.*, 1908, **41**, 2373, record m.p. 205°).

Cyclisation of 6-Methoxy-3-benzylcoumarilic Acid.—If the acid is cyclised through the acid chloride in cold CS_2 with $AlCl_3$, 3-methoxy-6-hydroxy-β-brazan is formed, as detected by typical colour reaction with chloroform and alkali. But the isolation of the pure material was not possible in any of the experiments. The crude sulphur-containing mass on oxidation with chromic acid in acetic acid gave 3-methoxy-β-brazanquinone which readily crystallised from pyridine in golden yellow plates, m. p. and mixed m.p. 292°. (Found : C, 73.2, 73.2 ; H, 3.8, 3.7. Calc. for $C_{17}H_{10}O_4$: C, 73.3 ; H, 3.6%). A better result was obtained when the cyclisation was done in benzene. The acid chloride (from acid, 2.0 g.) in benzene (20 c.c.) was cooled to 0° and treated with $AlCl_3$ (3 g.) and left overnight. On working up, a dirty solid product was obtained giving a positive colour reaction. This, on crystallisation from acetic acid, gave a product as colorless needles (0.15 g.), m. p. 225-26°, showing a negative colour reaction. (Found : C, 78.4, 78.4 ; H, 4.7, 4.9%). This compound is soluble in alkali, insoluble in sodium bicarbonate and gave a positive test for the methoxyl group and developed a yellow colour with H_2SO_4, turning to darkish pink. The mother-liquor was evaporated, the mass extracted with alkali and acidified. The amorphous mass was treated with warm alcohol, cooled and separated from a small quantity of crystals (the foregoing byproduct, m. p. 225°) and the filtrate allowed to evaporate slowly in a refrigerator. The crystals separating were collected (positive colour reaction with chloroform and alkali), pressed on the porous plate and crystallised from a small quantity of dilute alcohol, when *3-methoxy-6-hydroxy-β-brazan* was obtained in cream-coloured leaflets, m. p. 183-84°. This could not be analysed due to shortage of material.

2-Hydroxy-3 : 4-dimethoxyphenyl-(3' : 4'-dimethoxybenzyl) Ketone.—$AlCl_3$ (anhyd., 4 g.) was dissolved carefully in ice-cold dry ether (30 c.c.) and then 1 : 2 : 3-trimethoxybenzene (4.6 g.) was added to it in the cold. Homoveratroyl chloride (5.1 g.) in ether (15 c.c.) was added to the cooled stirred mixture. The violet colour which appeared at first changed to brown. After stirring for 4 hours in the cold, the mixture was left overnight and then decomposed after 30 hours. The *ketone*, isolated as usual, showed a violet ferric reaction. Crystallised from alcohol this was obtained in colorless needles (2.6 g.), m. p. 133-34°. (Found : C, 64.6 ; H, 6.2 ; $C_{18}H_{20}O_6$ requires C, 65.1 ; H, 6.0%).

6 : 7-Dimethoxy-3-(3' : 4'-dimethoxybenzyl)-coumarone-2-carboxylic Acid.—A mixture of the above ketone (3.1 g.), anhydrous acetone (40 c.c.), dry potassium carbonate (10 g.) and ethyl bromoacetate (4 c.c.) was refluxed for 6 hours. The oily product was taken up in ether, washed with sodium carbonate, dried and the solvent removed. Afte

removing the excess of ethyl bromoacetate in vacuum at 160°, the residue was dissolved in dry alcohol (20 c.c.) and added to alcoholic sodium ethoxide (sodium 0.4 g. and alcohol 10 c.c.) and refluxed for 1 hour. After removing most of the alcohol, the mixture was boiled with aqueous alcoholic sodium hydroxide (10 c.c., 10%) for ½ hour. On acidification a gum was obtained which solidified in contact with acetic acid. The *acid* was obtained as a chalky mass (1.8 g.) which, when crystallised from acetic acid, was obtained in wooly needles, m. p. 193-95°. With H_2SO_4 the compound gave a pink coloration. (Found : C, 63.9 ; H, 5.5. $C_{20}H_{20}O_7$ requires C, 64.5 ; H, 5.4%).

6 : 7-*Dimethoxy*-3-(3′ : 4′-*dimethoxybenzyl*)-2-*formylcoumarone*.—6 : 7-Dimethoxy-3-(3′ : 4′-dimethoxybenzyl)-coumarone was obtained as a glass (yield *ca.* 40%) by decarboxylating the above coumarilic acid by heating above its melting point with a trace of copper-bronze and distilling the product in vacuum. The crude product (0.4 g.) was dissolved in ether (10 c.c.) containing $ZnCl_2$ (0.3 g.), treated with anhydrous HCN (1 c.c.) and then saturated at 0° with HCl gas. The green sticky product was washed with dry ether, decomposed with hot water and the crude aldehyde obtained as a gum (0.25 g.), showing a red coloration with sulphuric acid and turning green immediately. The *dinitrophenylhydrazone* crystallised from acetic acid in red plates, m.p. 214°. (Found : N, 9.9. $C_{26}H_{24}O_9N_4$ requires N, 10.5%).

3 : 4 : 8 : 9-*Tetramethoxy-β-brazan* (II).—The crude aldehyde (0.2 g.), obtained above, was heated with syrupy phosphoric acid (5 c.c.) for 20 minutes at 100°. The mass became greenish and a crystalline product separated quickly. Water (20 c.c.) was added and the product collected and purified by chromatography on alumina in benzene solution. The violet fluorescent band (in U. V. light) was eluted with benzene (*ca.* 100 c.c.) and the crystalline *product* was obtained from acetic acid in colorless plates (0.17 g.), m. p. 244°. (Found : C, 71.6 ; H, 5.6. $C_{20}H_{18}O_5$ requires C, 71.0; H, 5.3%). With sulphuric acid the compound developed a green coloration.

o-*Hydroxyphenylbenzyl Ketone*.—A mixture of phenylacetonitrile (3.0 g.) and ethyl *o*-methoxybenzoate (3.8 g.) in benzene (20 c.c.) was added to alcohol-free sodium ethoxide (sodium, 0.5 g.) and refluxed for 4 hours. On cooling, the *sodium salt* of the keto-nitrile (III) separated. The mixture was treated with iced water, the aqueous layer separated and acidified to furnish the *keto-nitrile* in nearly quantitative yield, crystallising from alcohol in colorless prisms, m. p. 115°. (Found : N, 5.5. $C_{16}H_{13}O_2N$ requires N, 5.6%). The nitrile (2.0 g.) was dissolved in a mixture of HBr (10 c.c., 48%) and acetic acid (10 c.c.) and refluxed for 3 hours. The mixture was poured into water and cooled. The solid was collected and distilled in a current of steam. *o*-Hydroxyphenylbenzyl ketone was obtained from the distillate in a pure condition (1.0 g.), m.p. 59°, exhibiting a violet ferric reaction (Skraup and Binder, *Ber.*, 1929, **62**, 1127, record m.p. 57°). The residual solid in the flask was identified as 3-phenyl-4-hydroxycoumarin (V), which was crystallised from alcohol in colorless prisms or plates, m. p. 234° (Pauly and Lockemann, *Ber.*, 1915, **48**, 28, record m. p. 236° ; Stahmann *et al.*, *J. Amer. Chem. Soc.*, 1943, **65**, 2286, record m. p. 234-35°). (Found : C, 75.7 ; H, 4.4. Calc. for $C_{15}H_{10}O_3$: C, 75.6 ; H, 4.2%). The coumarin can also be extracted from an ethereal solution of the mixture with aqueous sodium carbonate. The *acetyl* derivative was

obtained in colorless needles, m. p. 182° from ethanol. (Found: C, 72.4; H, 4.7. $C_{17}H_{12}O_4$ requires C, 72.9; H, 4.3%). The *benzoyl* derivative (prepared in pyridine) was obtained in colorless plates, m. p. 205° from alcohol. (Found: C, 77.6; H, 4.1. $C_{22}H_{14}O_4$ requires C, 77.2; H, 4.1%).

3-Benzylcoumarone-2-carboxylic Acid.—The phenol (IV: 20 g.) was refluxed in dry acetone (150 c.c.) with potassium carbonate (55 g.) and ethyl bromoacetate (20 c.c.) for 7 hours. The phenoxyacetic ester, isolated with ether, was obtained as a colorless viscous oil which was next treated with alcoholic sodium ethoxide (sodium 3.0 g. and alcohol 260 c.c.) and refluxed for 1 hour. To this mixture was then added 5% NaOH (50 c.c.) and refluxed for another hour. Alcohol was removed by distillation and the residue acidified after dilution; the resulting gum was crystallised from glacial acetic acid, furnishing the *acid* (13.5-16.6 g.) as thick plates, m.p. 206°. (Found: C, 75.7; H, 5.0. $C_{16}H_{12}O_3$ requires C, 76.2; H, 4.8%). The compound developed gradually a reddish yellow colour with sulphuric acid. The *methyl ester*, prepared with methanolic H_2SO_4, crystallised from methanol in colorless prisms, m. p. 81-82° (labile, not obtained in subsequent experiments) and m.p. 123° (stable). (Found: C, 76.5; H, 5.2. $C_{17}H_{14}O_3$ requires C, 76.6; H, 5.2%). With diazomethane, the stable variety of the ester was isolated. The ester did not give any coloration with H_2SO_4. The *p-toluidide*, prepared by way of the acid chloride in benzene solution, was obtained in clusters of colorless needles, m. p. 253° from acetic acid and analysed for high nitrogen content. (Found: N, 5.6. $C_{23}H_{19}O_2N$ requires N, 4.1%).

3-Benzylcoumarone.—The above coumarilic acid could not be decarboxylated by heating above the melting point with copper-bronze; the original material was recovered. The acid (7 g.) was boiled with quinoline (35 c.c.) in presence of copper-bronze (0.5 g.) for 3½ hours, cooled, filtered, acidified and extracted with ether. The ether solution was washed successively with dilute acid and alkali, dried and distilled in vacuum. The product (1.1 g., recovered acid, *ca.* 4 g.) was obtained as a colorless liquid, b. p. 172-74°/4.2 mm, which solidified and obtained in prisms from methanol, m.p. 52°. (Chatterjea, this *Journal*, 1955, **32**, 265, records b. p. 170-75°/12 mm, which appears to be in error). The compound gave a yellow coloration with H_2SO_4. (Found: C, 86.0; H, 5.7. Calc. for $C_{15}H_{12}O$: C, 86.5; H, 5.8%).

Gattermann Reaction with 3-Benzylcoumarone.—The coumarone (1.0 g.) in pure dry ether (15 c.c.) was treated successively with $ZnCl_2$ (0.2 g.), $AlCl_3$ (anhyd., 0.5 g.), powdered KCl (0.1 g.) and HCN (1.5 c.c.) and saturated at 0° with dry HCl and left in the refrigerator for 2 days. There was no characteristic change in colour. A trace of a sticky material separating was washed with ether and then decomposed with water (4 c.c.) on the water-bath. A trace of *2-formyl-3-benzylcoumarone* was obtained which was isolated with ether and converted into *2:4-dinitrophenylhydrazone*, m. p. 244-45° from acetic acid. The sample was not analysed due to shortage of material.

Action of Hydrazine on Ethyl 3-Benzylcoumarone-2-carboxylate.—A mixture of the ester (5 g.), alcohol (25 c.c.) and hydrazine hydrate (12 c.c., 60%) was refluxed for 6 hours on the water-bath and then poured into water. The crystalline *product* (5 g.) was collected, crystallised twice from alcohol and obtained in colorless needles, m.p.

196°. {Found : C, 65.6, 65.7 ; H, 5.6, 5.6 ; N, 18.7. $C_{16}H_{14}O_2N_2$ (hydrazide) requires C, 72.2 ; H, 5.3 ; N, 10.5% ; $C_{16}H_{16}O_2N_4$ requires C, 64.9 ; H, 5.4 ; N, 18.8%}. The compound reduced Fehling's solution and gave on alkaline hydrolysis (2 hours), 3-benzylcoumarone-2-carboxylic acid, m. p. and mixed m.p. 206°. On interaction with benzenesulphonyl chloride in pyridine (using molecular proportions) a *sulphonhydrazide* was obtained, crystallising from methanol in transparent prisms (turning opaque on drying), m. p. 235°. (Found : N, 9.1%). Several experiments were carried out to decompose this sulphonhydrazide in ethyleneglycol with sodium carbonate, potassium carbonate and borax but no aldehyde could be detected in any of the experiments.

2-*Formyl*-3-*benzylcoumarone*.—3-Benzylcoumarone-2-carboxylic acid was converted into the N-*methylanilide* by the interaction of the acid chloride with methylaniline in boiling benzene for 8 hours. Crystallised from alcohol, the compound was obtained in colorless prisms, m. p. 148-49°, but the analysis was not satisfactory. (Found : N, 5.1. $C_{23}H_{19}O_2N$ requires N, 4.1%). A solution of the compound in tetrahydrofuran was carefully stirred and treated at the ordinary temperature with a solution of lithium aluminium hydride ($M/4$) in the same solvent. After stirring for 15 minutes, the mixture was carefully decomposed with HCl. The product obtained on working up contained a small quantity of the aldehyde which afforded the 2 : 4-*dinitrophenylhydrazone*, m.p. 244-45° (from acetic acid). (Found : C, 64 2 ; H, 4.2. $C_{22}H_{16}O_5N_4$ requires C, 63.5 ; H, 3.9%).

β-Brazan.—The crude aldehyde (0.08 g.) was boiled under reflux with a mixture of acetic acid (2 c.c.) and hydrobromic acid (1.5 c.c., 48%) for 3 hours. The product obtained on dilution was collected, dried and chromatographed on an alumina column. β-Brazan was obtained in a pure condition (*ca.* 4 mg.), m.p. 207-208° after crystallisation from benzene-alcohol. (Found : C, 87.9 ; H, 4.5. Calc. for $C_{16}H_{10}O$: C, 88.1 ; H, 4.5%).

2-*Acetyl*-3-*benzylcoumarone*.—3-Benzylcoumarone-2-carboxylic acid was converted into the *ketone*, following closely the method of Walker and Hauser (*loc. cit.*). The crude ketone was obtained as a gum which did not crystallise. The 2 : 4-*dinitrophenylhydrazone* crystallised from acetic acid in orange-red needles, m.p. 240-41°. (Found : N, 12.6. $C_{23}H_{20}O_5N_4$ requires N, 12.9%). The cyclodehydration of this compound with hydrobromic acid was not possible.

6-*Hydroxy*-β-*brazan*.—3-Benzylcoumarone-2-carboxylic acid (0.6 g.) was converted into the acid chloride in CS_2 solution (5 c.c.) with thionyl chloride (3 c.c.) and then the volatile materials were removed in vacuum. The oily residue was dissolved in CS_2 (25 c.c.), cooled in ice and gradually treated with excess of $AlCl_3$ (2 g.) and left overnight. After removing the solvent by decantation, the residue was decomposed with iced HCl and the crystalline product collected and washed with sodium carbonate solution. 6-*Hydroxy*-β-*brazan* (0.5 g.) crystallised from acetic acid in cream-coloured needles, m.p. 195°. (Found : C, 82.6 ; H, 4.6. $C_{16}H_{10}O_2$ requires C, 82.0 ; H, 4.3%). The compound developed a green coloration with chloroform and alkali.

The *acetyl* derivative crystallised from acetic acid in yellowish needles, m. p. 147°. (Found : C, 78.8 ; H, 4.3. $C_{18}H_{12}O_3$ requires C, 78.3 ; H, 4.3%).

On boiling this hydroxy compound (0.2 g.) with hydroidic acid (5 c.c., *d* 1.7) for 2 hours, *β*-brazan was obtained in excellent yield (0.15 g.), crystallising from benzene-alcohol in colorless plates, m. p. 207°.

β-Brazanquinone.—The foregoing hydroxy compound (0.2 g.) in boiling acetic acid (5 c.c.) was treated with a solution of chromic acid (0.25 g.) in water (1.2 c.c.), refluxed for 2 minutes and then the solution was cooled. The quinone was obtained in yellow needles, m. p. and mixed m.p. 242°. (Found : C, 77.3 ; H, 3.3. Calc. for $C_{18}H_8O_3$: C, 77.4 ; H, 3.2 per cent).

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POLYNUCLEAR AROMATIC HYDROCARBONS. PART IV. SYNTHESIS OF SOME 4-METHYL-1 : 2-BENZANTHRACENE DERIVATIVES

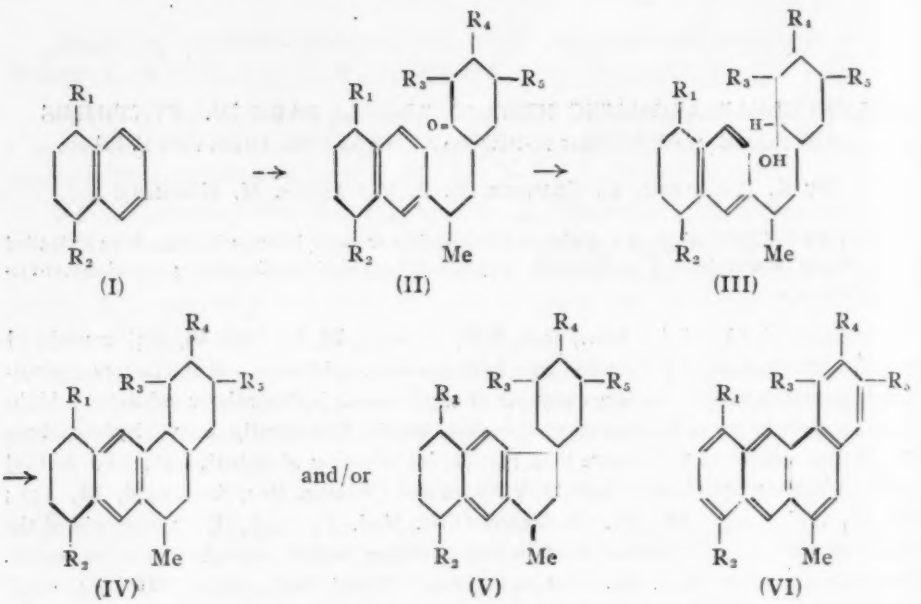
By R. P. Gandhi, K. Chander, O. P. Vig and S. M. Mukherji

The method of Mukherji for the synthesis of polynuclear aromatic hydrocarbons has been extended to the elegant synthesis of 1′ :4-dimethyl-, 2′ :4-dimethyl-, 3′ :4-dimethyl- and 4 :5 :8-trimethyl-1 :2-benzanthracenes.

Schmidt (*Z. physikal. Chem.*, 1938, **B39**, 59; 1938, **42**, 83; 1939, **44**, 194) considered that the distribution of π-electrons in a hydrocarbon might be one of the factors controlling biological activity. A large number of carcinogenic hydrocarbons exhibited a high-electron density area, designated as K-region, and in biologically active hydrocarbons this charge was found to be more than 1.293 *e*, introduction of substituents like methyl group enhancing the electron density (Pullman and Pullman, *Rev. Sci.*, 1946, **84**, 154 ; Dandel, *ibid.*, 1946, **84**, 37). Robinson (*Brit. Med. J.*, 1946, **1**, 943) associated the K-region with the 9 : 10-double bond in phenanthrene moiety, activated by substituents. But Pullmann *et al.* (*Bull. soc. chim.*, 1954, 1097; *Compt. rend.*, 1954, **238**, 964, 1935) have recently modified their earlier views on the minimum energetic index essential for carcinogenicity. They adumbrate, in addition to a favourable K-region, also an L-region. The former is postulated to be permissive or selective and the latter, exclusive. Woernly (*Arch. Biochem. Biophys.*, 1954, **50**, 199), however, regards the carcinogenic character as a result of overall electronic configuration rather than that of a specific region, although the latter may be one of the contributing factors.

However, these speculations regarding structural requirements in relation to carcinogenicity require more substantiation by semi-empirical quest. As a part of the programme of work in this direction, we have synthesised 1′ :4-dimethyl-, 2′ :4-dimethyl-, 3′ :4-dimethyl- and 4 : 5 : 8-trimethyl-1 : 2-benzanthracenes, which are all derivatives of 4-methyl-1 : 2-benzanthracene. In Part I (this *Journal*, 1955, **32**, 697) a very pliant method was described for the synthesis of 4-methyl-1:2-benzanthracene. In view of the fact that this compound is highly carcinogenic whereas the parent compound, 1:2-benzanthracene, is inactive, special importance attaches to our method for the fact that it leads directly to the 4-methyl-1:2-benzanthracene system.

2-Formyl-6-methyl*cyclo*hexanone was allylated and then hydrolysed, following essentially the conditions laid down by Mukherji and Bhattacharyya (*J. Org. Chem.*, 1952, **17**, 1202) for the preparation of 2-allyl*cyclo*hexanone, when 2-allyl-6-methyl*cyclo*hexanone was obtained in 54% overall yield. This was then subjected to aluminium chloride-catalysed reaction with tetralin (Part I, *loc. cit.*) to furnish (IIa) in 48% yield. The ketone (IIa) was reduced (Ponndorf) and the resulting alcohol (IIIa) was cyclised with concentrated sulphuric acid to (IVa) which was dehydrogenated with 30% palladised charcoal (*J. Chem. Soc.*, 1940, 1130) to 1′:4-dimethyl-1:2-benzanthracene (VIa) in 37% overall yield. No other isomeric aromatic products could be detected.



a: $R_1 = R_2 = R_4 = R_5 = H$; $R_3 = Me$
b: $R_1 = R_2 = R_3 = R_5 = H$; $R_4 = Me$
c: $R_1 = R_2 = R_4 = R_5 = H$; $R_5 = Me$
d: $R_3 = R_4 = R_5 = H$; $R_1 = R_2 = Me$

2-Allyl-5-methyl*cyclo*hexanone and tetralin, on the one hand, and 2-allyl*cyclo*hexanone and 1 : 4-dimethyltetralin, on the other, were similarly subjected to the above sequence of reactions, culminating in the synthesis of 2′ : 4-dimethyl-(VIb) and 4 : 5 : 8-trimethyl-1 : 2-benzanthracene (VId) in satisfactory overall yields. 2-Allyl-5-methyl*cyclo*hexanone was prepared by direct allylation of 3-methyl*cyclo*hexanone with sodamide and allyl iodide. The orientation in this reaction is formulated on the basis of analogy with carbethoxylation and formylation of 3-methyl*cyclo*hexanone (Kötz and Hesse, *Annalen*, 1905, **342**, 306; cf. Mukherji *et al.*, this *Journal*, 1956, **33**, 853).

The cyclisation of (III) admits of two possible products, the normal *cyclo*hexane structure (IV) or the spiran (V) or both (cf. *J. Amer. Chem. Soc.*, 1934, **56**, 959). As the objective of the present work was the synthesis of the fully aromatised systems, the proportion of the two possible structures in the cyclised product was not determined, because the spirans of the type (Vb) and (Vd) on dehydrogenation with 30% palladised charcoal would also furnish the fully aromatised system such as (VIb) and (VId) (cf. *ibid.*, 1955, **77**, 414 ; this *Journal*, 1952, **29**, 438 ; 1953, **30**, 27). But in the case of (Va), because of the dissymmetry of the *cyclo*hexane moiety, rearrangement on dehydrogenation should be expected to take place away from the methyl group due to steric interaction, resulting in the formation of the rearranged aromatised product (VIc) which, on the other hand, would be the normal product from 2-allyl-4-methyl*cyclo*hexanone when subjected to the above sequence of reactions, irrespective of whether cyclisation product

was composed preponderantly of the *cyclo*hexane structure (IVc) or of the spiran (Vc = Va). To throw light on this point, which would also determine whether cyclisation of (IIIa) proceeded perceptibly to the spiran (Va), we subjected 2-allyl-4-methyl*cyclo*hexanone and tetralin to the above sequence of reactions, when 3′:4-dimethyl-1:2-benzanthracene (VIc) was obtained in 38% overall yield. The mixed melting points of the aromatic hydrocarbons (VIa) and (VIc) showed considerable depression, indicating thereby that cyclisation of (IIIa) proceeded practically exclusively to the *cyclo*hexane structure (IVa) and not the spiran (Va).

The possibility of cyclisation of (IIIa), (IIIb), (IIIc) and (IIId) in the alternative direction at the position-5 in the tetralin moiety was ruled out on the basis of analogy with our synthesis of 4-methyl-1:2-benzanthracene and 1:4-dimethylanthracene (see Part I, *loc. cit.*). Also, partial cyclisation at position-5 would lead, through the above sequence of reactions, to some 1:4′-dimethyl-, 1:3′-dimethyl-, 1:2′-dimethyl- and 1:5:8-trimethyl-3:4-benzphenanthrene, which, however, could not be detected in the final aromatised products.

EXPERIMENTAL*

*2-Allyl-2-formyl-6-methyl*cyclo*hexanone*.—To an ice-cooled suspension of sodium ethoxide in benzene (prepared from 3.3 g. of pulverised sodium, 10 c.c. of absolute alcohol and 200 c.c. of dry benzene) was added dropwise with shaking 2-formyl-6-methyl*cyclo*hexanone (20 g.) (prepared in 65% yield from 2-methyl*cyclo*hexanone as in the case of 2-formyl-4-methyl*cyclo*hexanone, *vide infra*) and kept overnight, when the sodio-salt separated as an orange solid. The mass was cooled and allyl iodide (26 g.) added with shaking. After standing for an hour, the reaction mixture was refluxed on the steam-bath for 8 hours, when the supernatant layer gave no coloration with alcoholic ferric chloride solution. The mixture was treated with water and the benzene layer separated, washed with water and dried (Na_2SO_4). On removal of the solvent the desired product (16 g., 62.2%) came over at 90-95°/7 mm. (Found: C, 73.21; H, 8.57. $C_{11}H_{16}O_2$ requires C, 73.33; H, 8.88%).

*2-Allyl-6-methyl*cyclo*hexanone*.—The above formyl derivative (15 g.) was stirred for 4 hours at 50-55° with 5% KOH solution (150 c.c.). The hydrolysate was acidified with ice-cold HCl (dil.) and the organic product taken up in ether; the ethereal layer was washed with water and dried (Na_2SO_4). The residue, left after removal of the solvent, distilled at 82-85°/7 mm, yield 11 g. (86.8%). (Found: C, 78.68; H, 10.41. $C_{10}H_{16}O$ requires C, 78.90; H, 10.52%).

2-[*β-Methyl-β-(6′-tetralyl)-ethyl*]-6-*methyl*cyclo*hexanone* (IIa).—To freshly distilled tetralin (100 c.c.), ice-cooled in a 250 c.c. three-necked flask, fitted with a guard tube, a mercury-sealed mechanical stirrer and a dropping funnel, was added anhydrous $AlCl_3$ (17.5 g., 1*M*) in eight lots in 80 minutes. After the addition of each lot of $AlCl_3$, about 1 g. of 2-allyl-6-methyl*cyclo*hexanone was added (10 g. in all, 2*M*). The temperature was not allowed to rise above 5° during the addition. The reaction mixture was stirred for 5 hours at 0°-5° and then decomposed by ice-cold HCl and the product extracted with ether. The ethereal extract was washed free of acid and dried (Na_2SO_4).

* Melting and boiling points are uncorrected. Analyses by Drs. Weiler and Strauss, Oxford.

The solvent was removed and the residue on fractionation gave 9 g. (48%) of (IIa), b.p. 200-205°/5 mm. (Found: C, 84.15; H, 10.25. $C_{20}H_{28}O$ requires C, 84.50; H, 9.86%).

2-[*β-Methyl-β-(6'-tetralyl)-ethyl*]-6-*methyl*cyclo*hexanol* (IIIa).—The ketone (IIa: 7 g.) in *iso*propyl alcohol (40 c.c.) was reduced with aluminium *iso*propoxide (from 2.5 g. Al) and worked up in the usual manner. Distillation of the product furnished 6 g. (85%) of (IIIa) as a colorless viscous oil, b.p. 212-15°/6 mm. (Found: C, 83.44; H, 10.91. $C_{20}H_{30}O$ requires C, 83.91; H, 10.49%).

1′:4-*Dimethyl-dodecahydro*-1:2-*benzanthracene* (IVa).—The alcohol (IIIa: 5 g.) was treated with H_2SO_4 (7 c.c., *d* 1.84) in the cold (0°-5°) when 3 g. (64 %) of the dodecahydro derivative (IVa) was obtained, b.p. 177-80°/3 mm. (Found: C, 89.83; H, 10.29. $C_{20}H_{28}$ requires C, 89.55; H, 10.45%).

1′:4-*Dimethyl*-1:2-*benzanthracene* (VIa).—The above product (IVa: 2 g.) was heated with palladised charcoal (30%, 0.2 g.) for 4 hours at 300°-320°. The product was extraced with ether and the solvent removed. The residue was converted into its picrate which was purified by crystallisation from ethanol. The hydrocarbon (VIa) was regenerated from the purified picrate by treatment with dilute ammonia and was crystallised from benzene-ethanol mixture to obtain 1.3 g. (68%) of (VIa), m.p. 161°. (Found: C, 94.12; H, 6.67. $C_{20}H_{16}$ requires C, 93.75; H, 6.25%.

The *picrate* obtained as orange-red needles was crystallised from ethanol, m.p. 147°. (Found: N, 8.30. $C_{26}H_{19}O_7N_3$ requires N, 8.66%).

2-*Allyl*-5-*methyl*cyclo*hexanone*.—To sodamide prepared *in situ* (Vaughn *et al.*, *J. Amer. Chem. Soc.*, 1934, **56**, 2120) from 4 g. of sodium was added dry benzene (100 c.c.). 3-Methyl*cyclo*hexanone (20 g.) was then added dropwise to the well-stirred suspension of sodamide at 5°-10°. The mixture was stirred for 1 hour at room temperature (20°) and then heated on the steam-bath for a further period of 3 hours. It was then cooled at 0°-5° and allyl iodide (32 g.) was added dropwise. After standing for an hour the reaction mixture was refluxed on the water-bath for 8 hours. It was then cooled and decomposed and the aqueous portion extracted with ether. The combined extract was then washed with water and dried (Na_2SO_4). After removing the solvent, the product (14 g., 51.6%), distilling at 85°-90°/5mm, was collected. The ketone was characterised by its orange 2:4-dinitrophenylhydrazone, crystallised from ethyl acetate-ethanol mixture, m.p. 132-33°. (Found: N, 16.55. $C_{18}H_{20}O_4N_4$ requires N, 16.86%).

2-[*β-Methyl-β-(6'-tetralyl)-ethyl*]-5-*methyl*cyclo*hexanone* (IIb).—2-Allyl-5-methyl-*cyclo*hexanone (12 g.) was subjected to aluminium chloride-catalysed reaction with tetralin (120 c.c.) in the presence of finely powdered $AlCl_3$ (21.4 g.) according to the conditions laid down for the preparation (IIa), when 11 g. (49%) of the ketone (IIb), boiling at 205-208°/4mm, was obtained. (Found: C, 84.15; H, 10.46. $C_{20}H_{28}O$ requires C, 84.50; H, 9.86%).

2-[*β-Methyl-β-(6'-tetralyl)-ethyl*]-5-*methyl*cyclo*hexanol* (IIIb).—The ketone (IIb: 7 g.) in *iso*propyl alcohol (35 c.c.) was reduced with aluminium *iso*propoxide (from 2.5 g. Al) in the usual manner, when 6 g. (85%) of (IIIb) was obtained boiling at 200-202°/4mm. (Found: C, 84.12; H, 10.48. $C_{20}H_{30}O$ requires C, 83.91; H, 10.49%)

2′:4-*Dimethyl-dodecahydro*-1:2-*benzanthracene* (IVb).—The above alcohol (IIIb: 4 g.) was cyclised with H_2SO_4 (4 c.c., *d* 1.84) as in the case of (IIIa), when 2.5 g. (66.6%) of (IVb) came over at 182-85°/5 mm. (Found: C, 89.92; H, 10.36. $C_{20}H_{28}$ requires C, 89.55; H, 10.45%).

2′:4-*Dimethyl*-1:2-*benzanthracene* (VIb).—The product (IVb: 1.5 g.) was dehydrogenated with 30% palladised charcoal (0.15 g.) at 300°-320° for 4 hours. After working up in the usual way, the dehydrogenated product was converted into its picrate and the picrate, purified by crystallisation from ethanol, was decomposed with dilute ammonia. The regenerated hydrocarbon (VIb) was crystallised from benzene-ethanol mixture in colorless needles, m.p. 181°, yield 1 g. (70%). (Found: C, 93.30; H, 6.52. $C_{20}H_{16}$ requires C, 93.75; H, 6.25%).

The picrate of (VIb) was crystallished from ethanol as orange-red needles, m.p. 151-52°. (Found: N, 8.45. $C_{26}H_{19}O_7N_3$ requires N, 8.66%).

2-*Allyl*-2-*formyl*-4-*methyl*cyclo*hexanone*.—To a cooled suspension of sodium ethoxide (from 7 g. of sodium) in benzene (200 c.c.) was added ethyl formate (30 g.). After standing for 2 hours, 4-methyl*cyclo*hexanone (23 g.) in benzene (50 c.c.) was added with shaking; a yellow solid mass gradually separated. The mixture was allowed to stand for 6 hours after which it was decomposed with ice-water. The aqueous layer was acidified with ice-cold HCl, when an oil was obtained. On working up in the usual way, 17 g. (60%) of 2-formyl-4-methyl*cyclo*hexanone was obtained showing an intense violet coloration with alcoholic ferric chloride, b.p. 90°/5 mm.

The above formyl derivative (16 g.) was added in the cold to a solution of potassium (4.5 g.) in *tert.*-butyl alcohol (200 c.c.) and left overnight when potassium salt separated. To this solid mass was added, with ice-cooling, allyl iodide (22 g.), and the mixture after standing for an hour was refluxed on the steam-bath for 8 hours when it failed to exhibit any coloration with alcoholic ferric chloride. The reaction mixture was then diluted with water and extracted with benzene. After working in the usual way, 14 5 g. (70%) of 2-allyl-2-formyl-4-methyl*cyclo*hexanone was obtained as a clear liquid, b.p. 110-15°/5mm. (Found: C, 73 06; H, 8.72. $C_{11}H_{16}O_2$ requires C, 73.33; H, 8.88%).

2-*Allyl*-4-*methyl*cyclo*hexanone*.—The above formyl derivative (14 g.) was mechanically stirred for 4 hours with a 5% KOH solution (150 c.c.) at 50°-55°. It was then cooled and decomposed with iced HCl. After working up in the usual way, 2-allyl-4-methyl*cyclo*hexanone (10.5 g., 88%) was obtained as a mobile liquid, b.p. 95-98°/8mm. (Found: C, 78.42; H, 10.89. $C_{10}H_{16}O$ requires C, 78.90; H, 10.52%)

The 2:4-*dinitrophenylhydrazone*, prepared by the sulphuric acid method, was crystallised from alcohol, m.p. 85°. (Found: N, 16.70. $C_{16}H_{20}O_4N_4$ requires N, 16.86%).

2-[*β-Methyl-β-(6′-tetralyl)-ethyl*]-4-*methyl*cyclo*hexanone* (IIc).—2-Allyl-4-methyl-*cyclo*hexanone (10 g.) was treated with tetralin (100 c.c.) in presence of anhydrous aluminium chloride (18 g.), following the same conditions described in the case of (IIa), when 15 g. (80%) of (IIc) was obtained, b.p. 195-200°/5 mm., η_D^{25} 1.5672. (Found: C, 84.99; H, 9.40. $C_{20}H_{28}O$ requires C, 84.50; H 9.86%).

2-[*β-Methyl-β-(6′-tetralyl)-ethyl*]-4-*methyl*cyclo*hexanol* (IIIc).—The above ketone (IIc: 7 g.) was reduced with aluminium *iso*propoxide (prepared from 2.5 g. of Al),

in the same way as in (IIa), when 6 g. (85%) of the carbinol (IIIc) was obtained, b.p. 209-12°/5 mm., η_D^{25} 1.5630. (Found: C, 84 25; H, 9.98 $C_{20}H_{30}O$ requires C, 83.91; H, 10.49%).

3′:4-*Dimethyl-dodecahydro*-1:2-*benzanthracene* (IVc).—The above carbinol (5 g.) was stirred with H_2SO_4(conc., 5 c.c.) in the cold (0°) for 4 hours when 3.8 g. (80%) of the dodecahydro derivative (IVc) was obtained, b.p. 175-77°/3 mm., η_D^{25} 1.5712. (Found: C, 89.99; H, :0.02. $C_{20}H_{28}$ requires C, 89.55; H, 10.45%).

3′:4-*Dimethyl*-1:2-*benzanthracene* (VIc).—The dodecahydro derivative (IVc: 2 g.) was heated with 30% palladium-charcoal (0.2 g.) at 300°-320° for 4 hours. After working up in the usual manner, 1.4 g. of the aromatised product (VIc) was obtained which was crystallised from benzene-ethanol mixture as light yellow flakes, m.p. 145-46°; mixed m.p. with (VIa), 135-38°. (Found: C, 93.71; H, 6.29. $C_{20}H_{16}$ requires C, 93.75; H, 6.25%).

The *picrate*, prepared in the usual manner, was crystallised from ethanol as red needles, m.p. 179-80° (decomp.). (Found: N, 8.5, $C_{26}H_{19}O_7N_3$ requires N, 8.66%).

2-[*β-Methyl-β-*(1′:4′-*dimethyl-6′-tetralyl*)-*ethyl*]-cyclo*hexanone* (IId)—2-Allyl-*cyclo*hexanone (Mukherji and Bhattacharyya, *J. Org. Chem.*, 1952, **17**, 1202) (15 g.) was subjected to cationoid reaction with 1:4-dimethyltetralin (I: $R_1 = R_2 = Me$) (*idem*, *Science & Culture*, 1951, **16**, 374) (35 g.) in presence of anhydrous aluminium chloride (26.8 g.), following the conditions as described for the preparation of (IIa), when 12 g. (36.5 %) of the ketone (IId) was obtained, b.p. 200-205°/2mm. (Found: C, 84.87; H, 10.39. $C_{21}H_{30}O$ requires C, 84.51; H, 10.13%).

2-[*β-Methyl-β-*(1′:4′-*dimethyl-6′-tetralyl*)-*ethyl*]-cyclo*hexanol* (IIId).—The above ketone (IId: 7 g.) was reduced with aluminium *iso*propoxide (from 2.5 g. Al in 50 c.c. *iso*propyl alcohol) in the usual way, when 5 g. (83%) of the alcohol (IIId) was obtained as a colorless viscous oil, b.p. 210-15°/6 mm. (Found: C, 83.47; H, 10.26. $C_{21}H_{32}O$ requires C, 83.94; H, 10.73%).

4:5:8-*Trimethyl-dodecahydro*-1:2-*benzanthracene* (IVd).—The carbinol (IIId: 4 g.) was cyclised by the action of H_2SO_4 (4 c.c., *d* 1.84) as in the case of (IIIa), when 2.4 g. (63.7%) of the cyclised product (IVd) was obtained, b.p. 175-78°/5 mm. (Found: C, 89.71; H, 10.33. $C_{21}H_{30}$ requires C, 89.29; H, 10.71%).

4:5:8-*Trimethyl*-1:2-*benzanthracene* (VId).—The cyclised product (IVd: 2 g.) was dehydrogenated with 0.2 g. of 30% palladised charcoal at 300°-320° for 4 hours as in the case of (IVa). The hydrogenated product obtained after the usual working up was converted into its picrate which was purified through crystallisation from ethanol as dark red needles, m.p. 173°. (Found: N, 8.45. $C_{27}H_{21}O_7N_3$ requires N, 8.41%). The purified picrate was then decomposed with dilute ammonia and the regenerated hydrocarbon (VId) was crystallised from benzene-ethanol mixture to furnish 1.4 g. (73.7%) of the pure hydrocarbon (VId), m.p. 74-75°. (Found: C, 93.66; H, 6.52 $C_{21}H_{18}$ requires C, 93.29; H, 6.71%).

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ORGANIC REACTIONS WITH POLYPHOSPHORIC ACID. PART III. ONE-STEP ACYLATION AND ALKYLATION: *cyco*PENTENONES

By Sukh Dev

Polyphosphoric acid has been shown to be a useful reagent for the one-step synthesis of certain cyclic systems which had been prepared previously through several intermediate stages. Possible mechanistic features of the reaction have been discussed.

Nazarov and co-workers (*Bull. Acad. Sci. U. S. S. R., Cl. Sci. Chim.*, 1946, 633 ; 1947, 205 ; *J. Gen. Chem.*, U.S.S.R. 1950, **20**, 2009, 2079, 2091) have demonstrated that a variety of allylvinyl and divinyl ketones undergo an acid-catalysed ring-closure to yield substituted *cyclo*pentenones. The most useful reagent for this purpose has been found to be a phosphoric acid-formic acid mixture. It appeared that polyphosphoric acid (PPA) could be utilised with advantage for such Nazarov cyclisations. Since PPA had been shown to be capable of effecting intermolecular acylations (Sukh Dev, *Chem. & Ind.*, 1954, 1071 ; this *Journal*, 1956, **33**, 703) it was thought worthwhile to investigate the acylation of *cyclo*alkenes with suitable unsaturated acids, as the resulting primary products of acylation could possibly undergo ring-closure under the conditions of the reaction to furnish directly the substituted *cyclo*pentenones. This one-step acylation and alkylation reaction has been realised and forms the subject matter of the present communication (cf. Sukh Dev, *loc. cit.*, 1954).

The Friedel-Crafts reaction between an acid chloride of an $\alpha\beta$-unsaturated acid and an aromatic hydrocarbon is known to produce substituted *cyclo*pentenones in certain cases (Kohler, *Amer. Chem. J.*, 1909, **42**, 375 ; Auwers, *Ber.*, 1921, **54**, 987 ; Auwers and Risse, *Annalen*, 1933, **502**, 282 ; Baker and Jones, *J. Chem. Soc.*, 1951, 787 ; Herz, *J. Amer. Chem. Soc.*, 1953, **75**, 73). The same reaction, when carried out on an acid instead of its chloride, results in alkylation only (Eijkman, *Chem. Weekblad.*, 1907, **4**, 727 ; 1908, **5**, 655). The Friedel-Crafts interaction between a *cyclo*alkene and an unsaturated acid chloride leads to the formation of the corrseponding dichloroketones contaminated to some extent with the corresponding chlorovinyl ketones ; these intermediates resist cyclisation under the conditions of the reaction (Baddeley *et al.*, *J. Chem. Soc.*, 1953, 124).

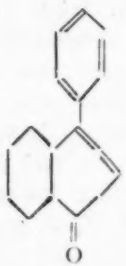
*Bi*cyclo-[4 : 3 : 0]-*nonane System*

On treatment of *cyclo*hexene with acrylic acid in PPA, the expected 4 : 5 : 6 : 7-tetrahydroindan-1-one (I) (Sukh Dev, this *Journal*, 1955, **32**, 255 and the references cited therein) was readily obtained in 16% yield. As anticipated, the reaction between crotonic acid and *cyclo*hexene was more facile and 3-methyl-4 : 5 : 6 : 7-tetrahydroindan-1-one (II) could be obtained in yields of 55-60%. This compound was obtained previously

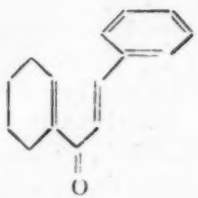
by Nazarov and Pinkina (*Bull. Acad. Sci. U.S.S.R., Cl. Sci. Chim.*, 1946, 633), and Hamlet *et al.* (*J. Chem. Soc.*, 1951, 2652) by the vinyl-acetylene method involving three steps; similarly Braude and Coles (*ibid.*, 1952, 1430) synthesised it by a new four-step reaction sequence in an overall yield of about 19%.

The condensation of cinnamic acid with *cyclo*hexene yielded a ketone in 25% yield. As will be clear from the reaction mechanism discussed below, this unsaturated ketone can possibly have a structure (III), (IV) or (V); the last structure represents the product of simple acylation. Since the product displayed its $\alpha\beta$ unsaturated ketone absorption peak at 238 mμ (ϵ 13150), which is almost the same as that of (I) (λ_{max} 237 mμ) or (II) (λ_{max} 238 mμ), the structure (III) has been assigned to this compound; the chromophore present in (IV) or (V) should show this band at about 280 mμ (cf. Kuhn and Staab, *Ber.*, 1954, **87**, 262).

(I : R = H;
(II : R = Me)
(III : R = Ph)

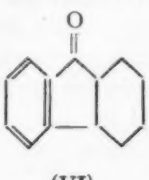


(IV)

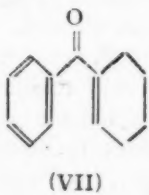


(V)

The reaction between benzoic anhydride and *cyclo*hexene afforded a ketone in 35-40% yield, which from its properties has been identified with the hexahydrofluorenone (VI) of Cook and Hewett (*J. Chem. Soc.*, 1936, 71; cf. Braude and Forbes, *ibid.*, 1953, 2208). To show the benzoyl*cyclo*hexene (VII) to be a possible intermediate, it was treated with PPA, when the cyclised ketone (VI) was obtained in 65% yield.



(VI)



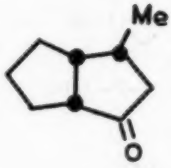
(VII)

Bicyclo-[3 : 3 : 0]-octane System

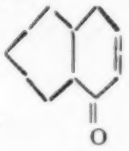
*cyclo*Pentene and crotonic acid react in the presence of PPA to yield a bicyclic ketone (22% yield), which has been characterised as 1-methyl-bi*cyclo*-[3 : 3 : 0]-$\Delta^{7:8}$-octen-3-one (VIII). This compound was obtained previously by Nazarov and Burmistrova (*Bull. Acad. Sci. U.S.S.R., Cl. Sci. Chim.*, 1947, 51) in an overall yield of

ca. 18% by a three-step sequence of reactions. The properties of this compound, as reported by these authors, are slightly different (vide Experimental) from those determined now. The structure (VIII) for our product is in accord with its U.V. light absorption (λ_{max} 241 mμ ; ϵ 12100).; an $\alpha\beta\beta$-trisubstituted *cyclo*pentenone is expected to display its principal band at 236 ± 5mμ (this *Journal*, 1955, **32**, 259 and the

(VIII)



(IX)



(X)

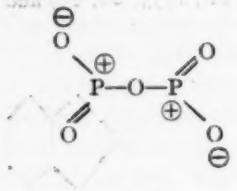
references cited therein). In the infra-red the compound showed peaks at 1665 cm^{-1} ($\nu_{C=O}$) and 1622 cm^{-1} ($\nu_{C=C}$), which are characteristic of an $\alpha\beta$-unsaturated ketone with a *transoid*-system (Jones and Sandorf in Weissberger's "Technique of Organic Chemistry", Interscience Publishers, 1956, Vol. IX, p. 481 ; Braude and Timmons, *J. Chem. Soc.*, 1955, 3766). As expected, the compound on quantitative catalytic hydrogenation consumed one mole equivalent of hydrogen to furnish a saturated dihydroketone (IX), which was stereochemically almost completely homogeneous. From the fact that the bi*cyclo*-[3 : 3 : 0]-octane system is far more stable in the *cis*-configuration (Cook and Linstead, *J. Chem. Soc.*, 1934, 946 ; Barrett and Linstead, *ibid.*, 1935, 438 ; 1936, 611) and that in catalytic hydrogenation at room temperature and pressure the hydrogen adsorbed on the surface of the catalyst effects a simultaneous *cis*-attack on the least sterically hindered side of the unsaturated substrate (Farkas and Farkas, *Trans. Faraday Soc.*, 1937, **33**, 837 ; Linstead *et al.*, *J. Amer. Chem. Soc.*, 1942, **64**, 1985), the dihydroketone has been assigned the *cis-syn* configuration (IX). In the infra-red the dihydroketone displayed its carbonyl stretching frequency at 1725 cm^{-1}. This value lies intermediate between those expected of a *cyclo*hexanone (1720 to 1706 cm^{-1}) and a *cyclo*pentanone derivative (1740 to 1749 cm^{-1} ; Bellamy, "The Infra-red Spectra of Complex Molecules", Methuen & Co., London, 1954, p. 127). The far less likely *cyclo*hexenone structure (X) * for the original condensation product has been ruled out by a straightforward synthesis of (VIII), accomplished in connection with some other investigation, to be reported later.

Discussion

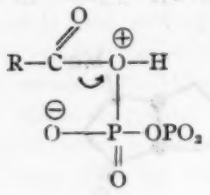
The activity of polyphosphoric acid for various acid-catalysed transformations and cyclisations (Uhlig, *Angew. Chem.*, 1954, **66**, 435) is undoubtedly due to the polar phosphorus pentoxide (XIV) made available in an ionising medium.

* Theoretically (cf. Discussion), the condensation of crotonic acid with *cyclo*pentene can possibly give rise to the *cyclo*hexenone derivative (X) : (Contd. next page).

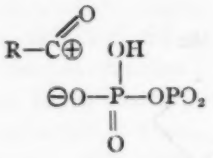
The dissolution of an organic acid in PPA should rapidly and reversibly lead to the formation of the preliminary co-ordination complex (XV), which stabilises itself by the electron-interactions indicated to give the ions shown in (XVI) ; it may be noted that the anion in (XVI) is stabilised by resonance.



(XIV)



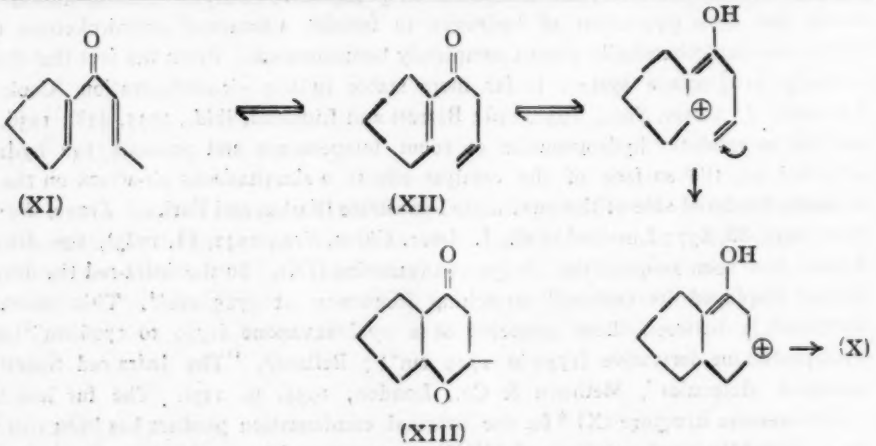
(XV)



(XVI)

Thus, a solution of an organic acid in PPA would be a potent source of acylium ions.

In the case of the results discussed in the present communication, the oxocarbonium ion (XVII) would be stabilised by resonance ; however the sterically-strained species (XVIIb) would not contribute appreciably. Its attack on an olefinic linkage should give the thermodynamically preferred intermediate (XVIII) **, which stabilises itself by the



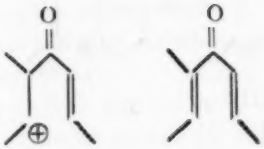
(XI) (XII) (XIII) → (X)

but this is unlikely as the equilibrium should be very largely in favour of (XI). It is of interest to note that both (XI; Braude and forbes, *J. Chem. Soc.*, 1953, 2208) and (XII; Nazarov and Burmistrova, *loc. cit.*) have been found to cyclise to (XIII) on treatment with phosphoric acid, and further that Braude and Forbes (*loc. cit.*) failed to effect the Nazarov cyclisation of (XI) to (VIII) with a mixture of phosphoric and formic acids.

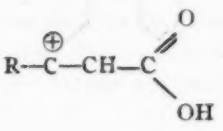
** That this carbonium ion has a fairly long life is indicated by its ability to undergo a Wagner-Meerwein type rearrangement wherever possible. Thus *cyclo*heptene and acetic or crotonic acid do not yield the normal expected products.

It may be further noted that (XVIII) can directly undergo ring-closure according to the Nazarov-Braude mechanism discussed later.

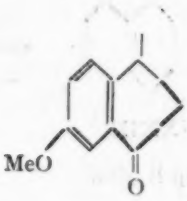
(XVII)



(XVIII) (XIX)



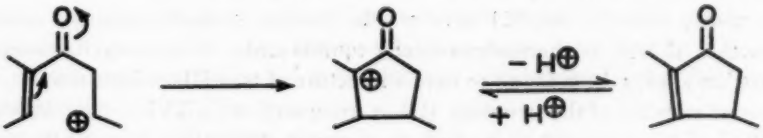
(XX)



(XXI)

elimination of a proton to yield the divinyl ketone (XIX). The fact that a carbonium ion of type (XX) is unimportant in these reactions conducted in PPA, is borne out by the results of the interaction of an unsaturated acid (e g. crotonic acid) and anisol. In this case only *p*-methoxycrotonophenone was obtained (80% yield) and none of 3-methyl-6-methoxyindan-1-one, which would have ultimately resulted from an attack of (XX), was detected (Sukh Dev, *loc. cit.*, 1956).

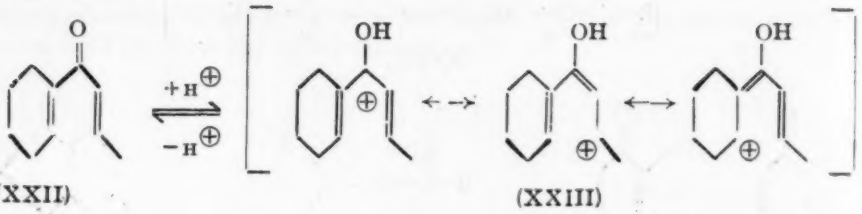
The divinyl ketone then undergoes ring-closure to yield the corresponding *cyclo*pentenone. Mechanism for the cyclisation of vinylallyl and divinyl ketones has been discussed (Nazarov and Kotlyarevskii, *J. Gen. Chem. U.S.S.R.*, 1950, **20**, 1501 ; Kursanov *et al.*, *Bull. Acad. Sci. U.S.S.R., Cl. Sci. Chim.*, 1953, 114 ; Braude and Coles, *J. Chem. Soc* , 1952, 1430). These authors assume the addition of the proton (in the case of the PPA, a proton or P_2O_5 itself can be considered as the active cyclising agent) to the propenyl or vinyl side-chain to give the carbonium ion (XXI) which cyclises as shown.



(XXI)

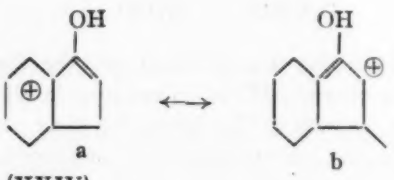
It can be seen that in the cyclisation of (XXI), the carbonium ion has attacked the electron-deficit end of the $\alpha\beta$-unsaturated carbonyl system, and as such, should not be very effective Moreover, the carbonyl oxygen is much more basic and it is known (Stoll and co-workers, *Helv. Chim. Acta*, 1955, **38**, 1573, 1593; 1956, **39**, 183, 200 ; Meinwald and Grossman, *J. Amer. Chem. Soc.*, 1956, **78**, 992) that if the resulting oxycarbonium ion (or its vinylog) is geometrically and sterically suitably situated with respect to the ethylenic linkage, it attacks it intramolecularly. In view of these considerations the following mechanism (cf. Erickson, M.I.T. Seminar in Organic Chemistry, 1954-55, 81 ; Braude and Coles, *loc. cit.*), which satisfies these points, appears more reasonable and is depicted for the cyclisation of crotonoyl-Δ^1-*cyclo*hexene (XXII) :

Step A (fast) :



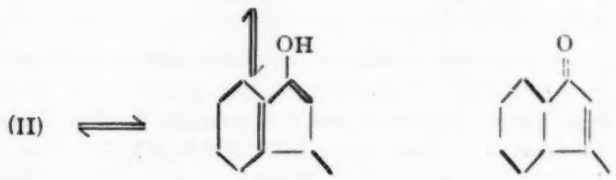
(XXII) (XXIII)

Step B (slow) :



(XXIV)

Step C (fast) :



(XXV) (XXVI)

In the cyclised carbonium ion (XXIV) the canonical structure (a) with a vacant *p*-orbital on a tertiary carbon should be of greater importance to the hybrid. Furthermore, since the step (C) is reversible, the final product under the conditions of the reaction should be thermodynamically equilibrated. In these cyclisations, the final product has always been found to have a structure of type (II), which should indicate a far greater stability of the structure (II) as compared to (XXVI) ; compounds of type (XXVI) have been isolated in cases where a proton-elimination to give the type (II) is not possible (Nazarov and Pinkina, *J. Gen. Chem.* U.S.S.R., 1950, **20**, 2079 ; Nazarov and Burmistrova *ibid.*, 1950, **20**, 2091).

EXPERIMENTAL

Melting and boiling points are uncorrected. Petroleum ether refers to the fraction of b.p. 40°-60°. Anhydrous sodium sulphate was used for drying the extracts. The ultraviolet light absorptions were measured in 95% ethanolic solution on a Beckman DU spectrophotometer.

4 : 5 : 6 : 7-*Tetrahydroindan-1-one* (I).—To PPA (from 70 g. of P_2O_5 and 30 c.c. of orthophosphoric acid of *d* 1.75 ; Sukh Dev, this *Journal*, 1955, **32**, 262), maintained at 57° ± 2° in a three-necked flask (250 c.c.) carrying a Hershberg stirrer and a reflux

condenser and protected from access of moisture, were introduced in one lot *cyclo*hexene (8.2 g., 0.1 *M*) and glacial acrylic acid (7.2 g., 0.1 *M*). The reaction mixture was vigorously stirred at that temperature for a total of 30 mins. The reddish brown product, while still hot, was at once poured on ice (*ca.* 200 g.) and water. After the decomposition of the complex, the mixture was diluted to 400 c.c. (*ca.*) with water and after dissolving in ammonium sulphate (75 g.) was extracted with petroleum ether (40 c.c. × 3). In case there was any polymerised material, insoluble in petroleum ether, that was rejected. The solvent extract was washed with water (50 c.c.), then with aqueous ammonium hydroxide (5% ; 50 c.c. × 2) and finally with brine (50 c.c.) and dried. The solvent was removed and the residue fractionated : after a forerun (0.3 g.) the desired ketone (I) was collected at 125-27°/12 mm (2.2 g., 16.2% ; n_D^{35} 1.5170) and a polymeric residue (*ca.* 7 g.) remained.

The ketone was characterised as its 2 : 4-*dinitrophenylhydrazone* (HCl method). Yield of the crude derivative of m.p. 221-24° was 85% ; recrystallisation from xylene gave dark red shining leaflets, m.p. 229-30° (Sukh Dev, *loc. cit.*, m.p. 229-30°), the m.p. remained undepressed on admixture with an authentic sample.

3-*Methyl*-4 : 5 : 6 : 7-*tetrahydroindan*-1-*one* (II).—When in the above experiment acrylic acid was replaced by an equivalent quantity of crotonic acid (8.6 g.) and the resulting dark red complex worked up as above, the bicyclic ketone (II) was obtained as a colorless oil, b.p. 152-55°/42 mm, n_D^{35} 1.5100, yield 9.0 g. (60%). The central cut of a refractionated sample had b.p. 130°/15 mm, 115°/4 mm, 106°/2.5 mm ; n_D^{35} 1.5105 ; λ_{max} 238 mμ (ε 13240) (Hamlet *et al.*, *loc. cit.*, record b.p. 84-86°/1 mm, n_D^{25} 1.5150 ; λ_{max} 238 mμ, ε 12500).

The *semicarbazone* (pyridine method) (m.p. of crude product, 209-212° decomp.) on two crystallisations from alcohol furnished white lustrous leaflets and flat needles, m.p. 216-17° (decomp.) (Braude and Coles, *loc. cit.*, record m.p. 214-17°).

The 2 : 4-*dinitrophenylhydrazone* (H_2SO_4 method) (m.p. of crude : 228-30°) on one crystallisation from acetic acid, followed by two recrystallisations from xylene, was obtained in dark red needles, m.p. 244° (decomp.) (Braude and Coles, *loc. cit.*, record m.p. 246-48° corr.).

3-*Phenyl*-4 : 5 : 6 : 7-*tetrahydroindan*-1-*one* (III) was similarly prepared by using finely powdered cinnamic acid (14.8 g., 0.1 *M*) in the above condensation. The complex was dark brown in colour and the product was extracted with ether (60 c.c. × 3) instead of petroleum ether. After a small forerun (0.5 g.), the required product was obtained as a viscous, pale yellow liquid of b.p. 162-65°/1.2 mm (n_D^{35} 1.5800 ; yield 5.5 g., 25.9%) and the polymeric residue amounted to 5 g. (*ca.*), (Found : C, 84.8 ; H, 7.8. $C_{13}H_{16}O$ requires C, 84.9 ; H, 7.54%).

The *semicarbazone* (pyridine method) (crude m.p. 214-15°) on three crystallisations from pyridine-alcohol mixture yielded colorless, transparent rectangular sheets, m.p. 220-21° with effervescence. (Found : N, 15.5. $C_{16}H_{19}ON_3$ requires N, 15.6%).

The 2 : 4-*dinitrophenylhydrazone* (HCl method) (crude m.p. 163-65°) was best recrystallised from benzene—*n*-hexane mixture to furnish red prismatic rods, m.p. 173-74°. (Found : N, 14.5. $C_{21}H_{20}O_4N_4$ requires N, 14.3%).

Hexahydrofluorenone (VI): (*i*) *From* cyclo*Hexene and Benzoic Anhydride.*—To PPA (P_2O_5, 70 g. and H_3PO_4, 30 c.c.) at 57° ±2° a mixture of *cyclo*hexene (8.2 g., 0.1 *M*) and benzoic anhydride (11.3 g., 0.05 *M*; the anhydride was preferred over the acid because of the much lower m.p. of the former) was added and the reaction carried out as described above. The complex was brown-red in colour and the extraction was carried out with ether. The crude product was fractionated first to get the cut of b.p. 115-25°/0.5 mm (9.0 g.), which was carefully refractionated, b.p. 118-22°/0.5 mm, yield 7.5 g. (41.6%). The product solidified on cooling in ice and was obtained in white prismatic rods by recrystallisation from petroleum ether at −10°, m.p. 42-42.5°, yield 2.8 g. The mother-liquor on working up yielded the crude ketone (4.3 g.) which gave the same semicarbazone (4.0 g., *vide infra*). Light absorption: λ_{max} 245 mμ (ε 12, 240) (Cook and Hewett, *loc. cit.*, record b.p. 126-29°/0.8 mm, m.p. 41.5-42°).

The *semicarbazone* (pyridine method) (crude: m.p. 203-205°) was recrystallised twice from alcohol to furnish white felted needles, m.p. 213-14° (Cook and Hewett, *loc. cit.*, record m.p. 212-13°).

The 2:4-*dinitrophenylhydrazone* (H_2SO_4 method) (crude: m.p. 185-88°) on crystallisation from acetic acid furnished brick-red, lustrous flat needles, m.p. 190-91° (Braude and Forbes, *loc. cit.*, record m.p. 190-91°).

(*ii*) *From Benzoyl-*Δ^1*-cyclo*hexene.—Benzoyl*cyclo*hexene was prepared by the method of Christ and Fuson (*J. Amer. Chem. Soc.*, 1937, **59**, 893). The material (b.p. 151-53°/6 mm, n_D^{31} 1.5580) prepared by this method could not be obtained in the crystalline state unlike the preparation of Braude and Forbes (*loc. cit.*). However, it could be purified *via* its *semicarbazido-semicarbazone*. This was prepared by allowing the ketone to react with two equivalents of semicarbazide hydrochloride in aqueous-alcoholic-pyridine solution; recrystallisation from dilute alcohol yielded colorless, prismatic rods and cubes, m.p. 206-207° with effervescence. (Found: N, 26.38, 26.42. $C_{15}H_{22}O_2N_6$ requires N, 26.42%). The regeneration of the ketone was effected by refluxing the well-powdered material (6.2 g.) with oxalic acid (10 g. in 200 c.c. of water) and *n*-heptane (50 c.c.) for 18 hours. Working up in that usual way yielded the ketone: b.p. 124°/0.75 mm, $n_D^{31.7}$ 1.5665, m.p. 37° (from pet. ether at −10°), yield 2.5 g., λ_{max} 246 mμ (ε 13080). 2:4-*Dinitrophenylhydrazone*, bright orange-red leaflets from benzene—*n*-hexane, m.p. 166-68° (Braude and Forbes, *loc. cit.*, record m.p. 38°, n_D^{31} 1.5660; λ_{max} 247 mμ, ε 12000; 2:4-dinitrophenylhydrazone m.p. 168°).

A mixture of PPA (from P_2O_5, 7 g. and phosphoric acid, 3 c.c.) and benzoyl*cyclo*hexene (1 g.) was heated on the steam-bath for 15 minutes and then worked up to yield the hexahydrofluorenone, b.p. 160-61°/4 mm, m.p. 41-42°, yield 0.65 g. Mixed m.p. with a sample from method (*i*) was undepressed.

3-*Methyl-bi*cyclo-[3:3:0]-$\Delta^{7:8}$*octen-1-one* (VIII).—To PPA (from P_2O_5, 70 g. and phosphoric acid, 30 c.c.) at 40° ± 2° *cyclo*pentene (6.8 g., 0.1 *M*) and crotonic acid (8.6 g., 0.1 *M*) were added and efficiently stirred at this temperature for one hour. The deep brownish red product was worked up as detailed for (I). The ketone was

obtained as a colorless liquid, b.p. 85-92°/3 mm, n_D^{20} 1.5010, yield 3.0 g. It was purified through its semicarbazone (*vide infra*) by the oxalic acid—*n*-heptane method (4½ hours' refluxing) to afford pure (VIII), b.p. 91-92°/4 mm, n_D^{19} 1.5045 (Nazarov and Burmistrova, *loc. cit.*, record b.p. 78-78.5°/4 mm., n_D^{22} 1.5060). (Found: C, 79.28 H, 8.91. $C_9H_{12}O$ requires C, 79.41 ; H, 8.9%).

The *semicarbazone* (pyridine method) (crude: m.p. 210-11°) was crystallised twice from a mixture of pyridine and alcohol to furnish colorless flat needles, m.p. 216-17° (decomp.) (Nazarov and Burmistrova, *loc. cit.*, record m.p. 201°). (Found: N, 22.1. $C_{10}H_{15}ON_3$ requires N, 21.8%).

The 2:4-*dinitrophenylhydrazone* (sulphuric acid method) was obtained as fine dark red needles from a mixture of acetic acid and alcohol, m.p. 214-15°. (Found: N, 17.9. $C_{15}H_{16}O_4N_4$ requires N, 17.7%[1].

3-*Methyl*-cis-*bi*cyclo-[3:3:0]-*octan*-1-*one* (IX).—The above ketone (3.1 g.) was hydrogenated at room temperature and pressure over prereduced Pd $CaCO_3$ catalyst (0.5 g.) in alcohol (25 c.c.). The hydrogen uptake ceased after (45 mins.) the absorption of 95% of the theoretical volume of hydrogen, when the catalyst was removed by filtration and washed with ether (50 c.c.). From the combined filtrates the solvents were fractionated off and the residue distilled to furnish the dihydroketone (IX) as a colorless liquid with a camphoraceous odour: b. p. 87-88°/9.5 mm, n_D^{20} 1.4700, yield 3.0 g. (Nazarov and Burmistrova, *loc cit.*, record b. p. 83-84°/11 mm, n_D^{21} 1.4738). (Found: C, 77.9 ; H, 10.1. $C_9H_{14}O$ requires C, 78.2; H, 10.1%).

The *semicarbazone* was prepared by the pyridine method (crude: m. p. 184-86°). Recrystallisation from dilute alcohol gave white needles, m.p. 186-87° (Nazarov and Burmistrova, *loc. cit.*, record m.p. 178-79°). (Found: N, 21.3. $C_{10}H_{17}ON_3$ requires N, 21.5%).

The 2:4-*dinitrophenylhydrazone* (HCl method) was crystallised from a mixture of benzene and *n*-hexane to furnish rosettes of orange-yellow needles, m.p. 161-62°. (Found: N, 17.2. $C_{15}H_{18}O_4N_4$ requires N, 17.6%).

Infra-red spectra were measured by the courtesy of Samuel P. Sadtler & Son Inc. (Philadelphia) on a Baird Associates I.R. spectrophotometer (NaCl prism) using pure liquids in 0.01 mm cell.

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ORGANIC REACTIONS WITH POLYPHOSPHORIC ACID. PART IV. INTRAMOLECULAR ACYLATION WITH LACTONES: *cyclo*PENTENONES FROM γ-LACTONES*

By Charanjit Rai and Sukh Dev

It has been demonstrated that the intramolecular acylation of suitably constituted γ-lactones to yield *cyclo*pentenones is best carried out with polyphosphoric acid.

A possible mechanism for the formation of γ-lactones by the action of alkylmagnesium halides on γ-keto-esters has been discussed.

Of the several routes available for the synthesis of *cyclo*pentenones (cf. Raphael in Rodd's "Chemistry of Carbon Compounds", Elsevier Publishing Co., Amsterdam, 1953, Vol. IIA, p. 95), the one utilising intramolecular acylation with lactones has certain attractive features. Apparently, Maschmeijer (Fr.P. 765, 515/1934; D.R.P. 667,156/1938; cf. Plattner and Pfau, *Helv. Chim. Acta*, 1937, **20**, 1474) was the first to record such a conversion, when he showed that undeca-lactone on treatment with concentrated sulphuric acid yielded 2-hexyl*cyclo*pentenone. Frank *et al.* (*J. Amer. Chem. Soc.*, 1944, **66**, 4; 1948, **70**, 3179; 1951, **73**, 724) later carried out the conversion of suitably constituted lactones to *cyclo*pentenones by flash-distilling them over phosphorus pentoxide. This procedure has been utilised by others in synthesis (La Forge and Barthel, *J. Org. Chem.*, 1945, **10**, 222; Sen Gupta and Datta, this *Journal*, 1948, **25**, 213; Gupta and Deshapande, *ibid.*, 1953, **30**, 23). A modification of the above method, which involves refluxing the lactone with P_2O_5 in a hydrocarbon solvent, has been preferred by some investigators (Ansell and Hey, *J. Chem. Soc.*, 1950, 2875; Mathieson, *ibid.*, 1951, 177), while Rothstein and Ficini (*Compt. rend.*, 1952, **234**, 1694) treated the lactone with P_2O_5 under reduced pressure. The conversion of lactones to *cyclo*pentenones has also been achieved by the zinc chloride-acetic acid-acetic anhydride reagent (Johnson *et al.*, *J. Amer. Chem. Soc.*, 1945, **67**, 1360, 1366; Mathieson, *loc. cit.*). Recently, excellent yields in the conversion of lactones to substituted 2-*cyclo*pentenones on heating with silica gel have been claimed (Bowles, U.S.P. 2, 623, 071/1952).

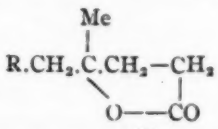
The above-mentoned procedures involving P_2O_5 result in a heterogeneous reaction mixture and furnish the desired *cyclo*pentenones in only moderate yields (20-50%). It was argued that a homogeneous reaction mixture obtainable with polyphosphoric acid (PPA) might result in superior yields. This has actually been found to be the case, and the present communication describes these results.

γ-*Lactones*

The γ-lactones of type (I) required for this investigation were prepared by the action of the requisite alkylmagnesium halide on ethyl laevulinate (Cason *et al.*, *Amer. Chem. Soc.*, 1944, **66**, 1765 and the references cited therein; Arnold and

* A preliminary note appeared in *Experientia*, 1955, **11**, 114.

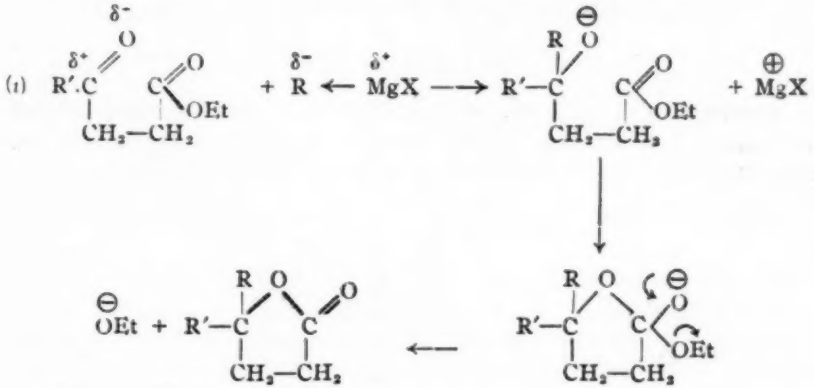
co-workers, *ibid.*, 1947, **69**, 2323 ; 1949, **71**, 1782 ; Frank *et al.*, *ibid.*, 1948, **70**, 1380) using the low-temperature technique of Cason *et al.* (*loc. cit.*).



(I)

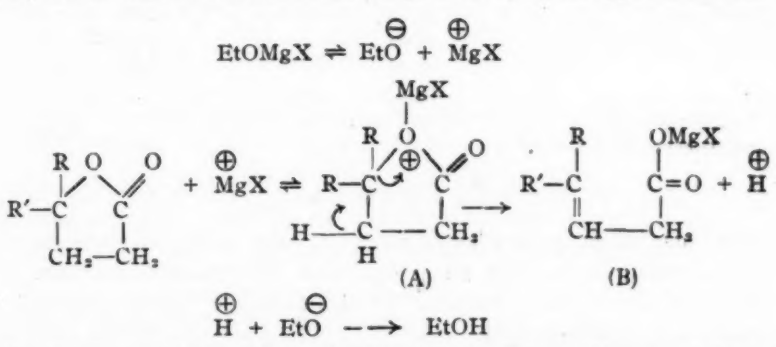
a : R = C_2H_5
b : R = n-C_3H_7
c : R = n-C_4H_9
d : R = n-C_5H_{11}
e : R = n-C_6H_{13}

This one-step formation of a γ-lactone by the interaction of a γ-keto-ester with a Grignard reagent* is most likely to take the following mechanistic path :



(*ii*) $\overset{\oplus}{MgX} + \overset{\ominus}{OEt} \rightleftharpoons EtOMgX$

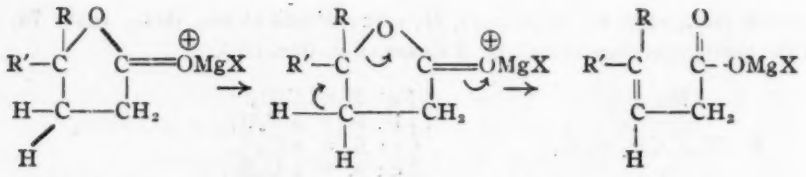
In some cases (Kloetzel, *J. Amer. Chem. Soc.*, 1940, **62**, 1708 ; Campbell and Soffer, *ibid.*, 1942, **64**, 417 ; Sukh Dev, this *Journal*, 1948, **25**, 69, 315) the corresponding βγ-unsaturated acid has been isolated as the chief product of the reaction. This can possibly result* from the co-ordination complex (A) by an E2-type elimination :



(A) (B)

* In this scheme only the typical nucleophilic character (Evans and Pearson, *J. Amer. Chem. Soc.*, 1942, **64**, 2865 ; Swain, *ibid.*, 1947, **69**, 2305 ; cf Roberts and Shoppee, *J. Chem. Soc.*, 1954, 3418) of the Grignard reagent has been stressed.

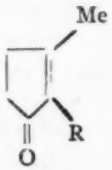
* The Referee pointed out the following alternative path : (see next page top).



Working up of the reaction mixture with an acid will generate the $\beta\gamma$-unsaturated acid from (B). From these considerations it can be deduced that a lower temperature of reaction and a less ionising reaction medium should favour the termination of the reaction at the lactone stage. This is well demonstrated by the work of Cason *et al.* (*loc. cit.*), who have prepared γ-lactones by this method in high yields.

cyclo*Pentenones*

On treatment with PPA the γ-lactones (I) were smoothly converted into the *cyclo*pentenones (II) in excellent yields. Table I depicts in a comparative manner the yields of the *cyclo*pentenones as obtained by the P_2O_5 and PPA methods.



(II)

a: R = Et
b: R = *n*-C_3H_7
c: R = *n*-C_4H_9
d: R = *n*-C_5H_{11}
e: R = *n*-C_6H_{13}

TABLE I

*cyclo*Pentenone (II).	% Yield by PPA method.	% Yield by P_2O_5 method.
a	90-92	...
b	92-97	32*
c	92-95	30†
d	92-95	50‡‡ 62‡
e	92-94	63††

* Frank *et al.* (1948, *loc. cit.*).
‡‡ Frank *et al.* (1944, *loc. cit.*).
†† Gupta and Deshapande (*loc. cit.*).
† La Forge and Barthel (*loc. cit.*).
‡ Rothstein and Ficini (*loc. cit.*).

EXPERIMENTAL

All melting and boiling points are uncorrected. The ultraviolet spectra were measured in 95% ethanolic solution on a Beckman DU spectrophotometer. The 2:4-dinitrophenylhydrazones were prepared by the sulphuric acid method and the semicarbazones by the pyridine method.

γ-Methyl-γ-alkylbutyrolactones (I).—In a special apparatus the requisite Grignard reagent was prepared from magnesium (2.43 g., 0.1 g. atom), alkyl bromide (0.015 *M*) and anhydrous ether (60 c.c.). Two-thrids of the ether was distilled off, the residue

diluted with dry, thiophene-free benzene (40 c.c.) and the solution forced by N_2 pressure into a dropping funnel, fitted to a 3-necked flask carrying a stirrer and containing ethyl laevulinate (14.4 g., 0.1 *M*) and benzene (100 c.c.). The Grignard reagent was added dropwise with stirring at -10 to 0° during 2 hours. After stirring for an additional ½ hour at the same temperature, the product was poured on ice and H_2SO_4 (C.P., 10 c.c.) and worked up as described by Cason *et al.* (*loc. cit.*). The properties of the lactones, thus prepared, are shown in Table II.

TABLE II

Lactone (I).	B.P.	$n_D^{25°}$.	Yield.	Lit. (*loc. cit.*)	B.P./n_D/*t*.	Yield.
a	126-27°/20 mm.	1.4397	55%	Cason *et al.*	128-29°/15 mm	73.3%
b	118-19°/8	1.4423	60	Frank *et al.* (1948)	85-87°/2 mm 1.4452/20°	60
c	129-31°/13	1.4447	60	LaForge & Barthel	98-100°/2 mm 1.4478/23°	...
d	159-60°/18	1.4460	60	Frank *et al.* (1944)	120-25°/4.5 mm 1.4487/20°	31
e	165-67°/12.5	1.4482	62	Gupta & Deshapande	146-48°/12 mm	23

3-*Methyl*-2-*alkyl*-Δ^2-cyclo*penten*-1-*one* (II): *General Procedure*.—To PPA (from P_2O_5 20 g. and 85% syrupy phosphoric acid 12 c.c. Sukh Dev, *loc. cit.*, 1955) maintained at 97° (boiling water-bath) the γ-lactone (0.02 *M*) was added, well-mixed with a glass rod and the coloured reaction mixture heated at the same temperature (with occasional mixing) under anhydrous conditions for 2½ hours. The deep red product, while still hot, was poured on ice (*ca.* 200 g.) and after the complex had decomposed, the organic material was taken in petroleum ether (50 c.c. × 4), washed with water (40 c.c.), brine (40 c.c. × 2) and dried (Na_2SO_4). The solvent was carefully fractionated off and the crude ketone, thus obtained, was rectified under vacuum. The relevant data are given below:

3-*Methyl*-2-*ethyl*-Δ^2-cyclo*penten*-1-*one* (IIa): b. p. 95-96°/18 mm, 86-87°/10 mm, $n_D^{29°}$ 1.4780; λ_{max} 234 mμ (ε 13,200). (Found: C, 77.3; H, 9.8. $C_8H_{12}O$ requires C, 77.4; H, 9.7%).

The 2:4-*dinitrophenylhydrazone* crystallised from alcohol in deep red needles, m.p. 186°. (Found: N, 18.2. $C_{14}H_{16}O_4N_4$ requires N, 18.4%).

3-*Methyl*-2-n-*propyl*-Δ^2-cyclo*penten*-1-*one* (IIb): b.p. 105°/17 mm, $n_D^{29°}$ 1.4775; *semicarbazone* (white crystalline nodules from alcohol) m. p. 210-11° (Hunsdiecker, *Ber.*, 1942, **75**, 455, records b.p. 94.5°/11.5 mm, m.p. of semicarbazone, 212°).

The 2:4 *dinitrophenylhydrazone* was obtained in deep red flat needles from alcohol, m.p. 182°. (Found: N, 17.4. $C_{15}H_{18}O_4N_4$ requires N, 17.6%).

3-*Methyl*-2-n-*butyl*-Δ^2-cyclo*penten*-1-*one* (IIc) (*Dihydrocinerone*): b.p. 124-25°/20 mm, 115-16°/10 mm, $n_D^{29°}$ 1.4775; λ_{max} 234 mμ (ε 12730); *semicarbazone* (white microcrystalline powder from alcohol) m.p. 191-92°; 2:4-*dinitrophenylhydrazone* (red,

long flat needles from alcohol) m.p. 153-5° (LaForge and Barthel, *loc. cit.*, record b.p. 107°/17 mm, n_D^{25} 1.4798 ; m. p. of *semicarbazone*, 191.5-92.5°, m.p. of 2 : 4-*dinitrophenylhydrazone*, 154-55°).

3-*Methyl*-2-n-*amyl*-Δ^2-cyclo*penten*-1-*one* (IId) (*Dihydrojasmone*, *Tetrahydropyrethrone*) : b. p. 138-39°/20 mm, 127-28°/10 mm, n_D^{25} 1.4760 ; *semicarbazone* (white, microcrystalline powder from alcohol) m.p. 175-76° ; 2 : 4-*dinitrophenylhydrazone* (bright red needles from alcohol) m.p. 123° (Treff and Werner, *Ber.*, 1933, **66**, 1525, record b.p. 101-102°/5 mm, n_D^{15} 1.48107 ; m.p. of semicarbazone 175-76°. Crombie *et al.*, *J. Chem. Soc.*, 1950, 3563, record m.p. of the 2 : 4 dinitrophenylhydrazone as 122°).

3-*Methyl*-2-n-*hexyl*-Δ^2-cyclo*penten*-1-*one* (IIe) : b.p. 145-47°/20 mm, 137-38°/10 mm, n_D^{25} 1.4735 ; λ_{max} 234 mμ (ϵ 12060) (Hunsdiecker, *loc. cit.*, records b. p. 142°/18 mm).

The 2 : 4-*dinitrophenylhydrazone* on crystallisation from alcohol furnished red needles, m.p. 135°. (Found : N, 15.3. $C_{18}H_{24}O_4N_4$ requires N, 15.5%).

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THERMODYNAMICS OF SOLUTIONS OF MIXED ELECTROLYTES

By K. T. Rama Varma

The thermodynamical treatment, developed by Srivastava and Rastogi (*Proc. Nat. Inst. Sci., India*, 1953, **19**, 613), has been extended to multi-component ionic solutions.

While the thermodynamics of solutions of single electrolytes has been extensively treated (Guggenheim, "Thermodynamics", 1952 ; Harned and Owen, "The Physical Chemistry of Electrolytic Solution", 1943), the development of a thermodynamic theory for solutions of several electrolytes seems not to have received sufficient attention. In this paper an attempt has been made to extend the treatment developed by Srivastava and Rastogi (*Proc. Nat. Inst. Sci. India*, 1953, **19**, 613) to multi-component ionic solutions.

Condensed Phase in Equilibrium with Non-ideal Vapour

We will discuss the conditions of equilibrium in a system containing electrolytes 1, 2, ... i ..... k (all binary) having no common ion dissolved in a solvent. We will denote the degrees of dissociation of these electrolytes by $\alpha_1, \alpha_2, \alpha_3, \ldots \alpha_i \ldots \alpha_k$. If $n_1, n_2, n_3 \ldots n_i \ldots n_k$ moles of the electrolyte are dissolved in n_s moles of the solvent, the number of moles of the different species of ions formed can be found out as follows:— n_i moles of the electrolyte i, when dissolved, will give $\alpha_i Z_{ia} n_i$ moles of anion, $\alpha_i Z_{ic} n_i$ moles of cation and $(1-\alpha_i)n_i$ moles of the undissociated electrolyte, where Z_{ia} and Z_{ic} are the number of anions and cations respectively formed from one mole of the electrolyte, if we assume the dissociation to be complete. We will thus have $\sum_i \alpha_i Z_{ia} n_i$ moles of anions, $\sum_i \alpha_i Z_{ic} n_i$ moles of cations, and $\sum_i (1-\alpha_i) n_i$ moles of undissociated electrolytes. The condition of electroneutrality is automatically satisfied from our basic assumption of the mechanism of dissociation and, hence, will not form a further restrictive condition. The mole fraction of the anion i will be given by

$$N_{ia} = \frac{\alpha_i Z_{ia} n_i}{\sum_{i=1}^{i=k} (\alpha_i Z_{ia} n_i + \alpha_i Z_{ic} n_i + \overline{1-\alpha_i} n_i) + n_s} \quad \ldots \quad \ldots \quad (1)$$

The mole fraction of the cation i will be given by

$$N_{ic} = \frac{\alpha_i Z_{ic} n_i}{\sum_{i=1}^{i=k} (\alpha_i Z_{ia} n_i + \alpha_i Z_{ic} n_i + \overline{1-\alpha_i} n_i) + n_s} \quad \ldots \quad \ldots \quad (2)$$

and the mole fraction of the undissociated electrolyte i will be given by

$$N_{iu} = \frac{(1-\alpha_i)n_i}{\sum_{i=1}^{i=k}(\alpha_i Z_{ia} n_i + \alpha_i Z_{ic} n_i + \overline{1-\alpha_i} n_i) + n_s} \quad \ldots \quad \ldots \quad (3)$$

Thus, we will have $3k+1$ species in the solution including the solvent which will have mole fractions denoted by N_{1a}, N_{1c}, N_{1u} ; N_{2a}, N_{2c}, N_{2u} ; ... .. ; N_{ia}, N_{ic}, N_{iu} ; ..... ; N_{ka}, N_{kc}, N_{ku} ; N_s. Out of these, however, not all will be independent, for we have the following relation between the mole fractions of the species formed from the same source i

$$\frac{N_{ia}S}{\alpha_i Z_{ia}} = \frac{N_{ic}S}{\alpha_i Z_{ic}} = \frac{N_{iu}S}{(1-\alpha_i)} = n_i, \quad \ldots \quad \ldots \quad (4)$$

where S represents the denominator in equations (1), (2) and (3).

Further, we have the relationship

$$\sum_i (N_{ia} + N_{ic} + N_{iu}) + N_s = 1 \quad \ldots \quad \ldots \quad \ldots \quad (5)$$

so that, in all, the mole fractions of only k species will be independent.

In the foregoing, we have assumed that the degrees of dissociation of the electrolytes α_1, α_2 ... α_i ... α_k do not vary with the concentration and temperature within a small range. This may be assumed to be approximately true of small changes in concentration, but the applicability of the equations derived below will be limited because of this restriction.

The general equation for liquid-vapour equilibrium can hence be represented as (Srivastava and Rastogi, *loc. cit.*):

$$-\left\{\frac{N_s L_s}{T}dT + \sum_{i=1}^{k}\frac{N_{ic}L_{ic}}{T}dT + \sum_{i=1}^{k}\frac{N_{ia}L_{ia}}{T}dT + \sum_{i=1}^{k}\frac{N_{iu}L_{iu}}{T}dT\right\}$$

$$+ N_s'\overline{V}_s dP + \sum_{i=1}^{k} N_{ic}\overline{V}_{ic}'dP + \sum_{i=1}^{k} N_{ia}\overline{V}_{ia}'dP + \sum_{i=1}^{k} N_{iu}\overline{V}_{iu}'dP$$

$$= -\left\{N_s \sum_{i=1}^{k}\left(\frac{\delta\mu_s'}{\delta N'_{ia}}\right)_{T,P,N'_{js}} \cdot \delta N'_{ia} + N_{ia}\sum_{i=1}^{k}\left(\frac{\delta\mu_{ia}'}{\delta N'_{ia}}\right)_{T,P,N'_{js}} \cdot dN_{ia}'\right.$$

$$\left. + N_{ic}\sum_{i=1}^{k}\left(\frac{\delta\mu_{ic}'}{\delta N_{ia}'}\right)_{T,P,N'_{js}} dN'_{ia} + N_{iu}\sum_{i=1}^{k}\left(\frac{\delta\mu'_{iu}}{\delta N_{ia}'}\right)_{T,P,N_{js}'} dN'_{ia} + \ldots \text{to } 3k+1 \text{ terms}\right\} \ldots \quad (6)$$

since for each electrolyte, we have to consider the mole fraction of only one of the three species as independent. We have here considered the mole fraction of the anion as independent ; but it makes no difference if we consider the mole fraction of the cation or that of the undissociated electrolyte as independent.

We shall also obtain in a similar way

$$-\frac{1}{T}\Big\{N'_1L_1+\sum_{i=1}^{k}N'_{ic}-L_{ic}+\sum_{i=1}^{k}N'_{ia}L_{ia}+\sum_{i=1}^{k}N'_{iu}L_{iu}\Big\}\,dT$$

$$+\Big\{N'_1\overline{V}'_1+\sum_{i=1}^{k}N'_{ic}\overline{V}'_{ic}+\sum_{i=1}^{k}N'_{ia}\overline{V}'_{ia}+\sum_{i=1}^{k}N'_{iu}\overline{V}'_{iu}\Big\}\,dP$$

$$=\Big\{N'_1\sum_{i=1}^{k}\Big(\frac{\delta\mu_1}{\delta N_{ia}}\Big)_{T,P,N_{ja}}dN_{ia}+N'_{ia}\sum_{i=1}^{k}\Big(\frac{\delta\mu_{ia}}{\delta N_{ia}}\Big)_{T,P,N_{ja}}dN_{ia}$$

$$+N'_{ic}\sum_{i=1}^{k}\Big(\frac{\delta\mu_{ic}}{\delta N_{ia}}\Big)_{T,P,N_{ja}}dN_{ia}+N'_{iu}\sum_{i=1}^{k}\Big(\frac{\delta\mu_{iu}}{\delta N_{ia}}\Big)_{T,P,N_{ja}}dN_{ia}+\ldots\text{to } 3k+1\text{ terms}\Big\} \quad \ldots \quad (7)$$

If we assume all the other species to be non-volatile except the solvent, which is usually the case, equation (7) reduces to the very simple form

$$-\frac{1}{T}N'_1L'_1\,dT+\overline{V}'_1\,dP=N'_1\sum_{i=1}^{k}\Big(\frac{\delta\mu_1}{\delta N_{ia}}\Big)_{T,P,Nja}dN_{ia} \quad \ldots \quad \ldots \quad (8)$$

or
$$-\frac{1}{T}\Big\{L_1^\circ-(H'_1-H_1^\circ)\Big\}dT+\overline{V}'_1\,dP=+\sum_{i=1}^{k}\Big(\frac{\delta\mu_1}{\delta N_{ia}}\Big)_{T,P,Nja}dN_{ia} \quad (8')$$

For a non-ideal solution, the chemical potential of the solvent is given by the relation

$$\mu_1=\mu_1^\circ+RT\ln a_1 \quad \ldots \quad \ldots \quad \ldots \quad (9)$$

where μ_1° depends on temperature and pressure and a_1 is the activity of the solvent. Using equation (9) we obtain from equation (8')

$$-\frac{1}{T}\Big\{L_1^\circ-(H'_1-H_1^\circ)\Big\}dT+\overline{V}'_1\,dP=RT\sum_{i=1}^{k}\Big(\frac{\delta\ln a_1}{\delta N_{ia}}\Big)_{T,P,Nja}dN_{ia} \quad \ldots \quad (10)$$

This equation can be used to express the variations of boiling point with pressure and composition and of total pressure with composition and so on.

The applicability of this equation, however, is limited because of the approximation already mentioned (that the degree of dissociation does not change with concentration). We shall hence derive formulae assuming complete dissociation of all the electrolytes. This will, in general, be true of strong electrolytes in dilute solutions. Although it is an oversimplification, it is a better model than the one which ignores dissociation into ions. We shall not henceforth distinguish between the different species of electrolytes, but only between the different species of ions. Accordingly, we can describe the compositions of solutions of electrolytes in terms of the molality m_i of each of the ionic species. Since the solution is electrically neutral, we have the following condition of electroneutrality

$$\sum_i Z_i m_i = 0$$

where the symbol Z_i denotes the charge on an ion i measured in units of the charge of a proton. Owing to this restrictive condition, a solution, containing $\gamma + 1$ species including the ionic species and the solvent has only γ independent components. If, however, the composition is expressed in mole fraction or ion fraction, we shall have only γ-1 independent components.

Assuming that all the other species are non-volatile except the solvent, we hence obtain

$$-\frac{1}{T}\left\{L_1^\circ-(H_1'-H_1^\circ)\right\}dT+\bar{V}_1'\,dP=\sum_{i=1}^{\gamma-1}\left(\frac{\delta\mu_1}{\delta N_i}\right)_{T,P,Nj}\delta N_i \qquad \ldots\ (11)$$

where the subscript 1 represents the solvent.

Since $$\mu_1=\mu_1^\circ+RT\ln a_1$$

we have $$-\frac{1}{T}\left\{L_1^\circ-(H_1'-H_1^\circ)\right\}dT+\bar{V}_1'\,dP=RT\,\Delta\ln a_1 \qquad \ldots\ (12)$$

Equation (12) expresses, for constant composition

$$\bar{V}_1'\,dP=-\frac{1}{T}\left\{L_1^\circ-(H_1'-H_1^\circ)\right\}dT \qquad \ldots \qquad \ldots\ (13)$$

If the vapour is assumed to be ideal, the above equation can easily show that when log P is plotted against temperature, a straight line should be obtained, with the help of which the heat of dilution can be computed.

It may be pointed out at this stage that the activity of the solvent can be computed from experimental values of boiling point elevations or freezing point depressions and compared with theoretical expressions. It need not be stressed that the above treatment holds good for solid-liquid equilibrium as well.

Solution of Single Electrolyte in Equilibrium with Non-ideal Vapour

In deriving most of the formulae for solutions of non-electrolytes, it is usually assumed that the solvent behaves as a perfect gas in the vapour phase. Here we shall depart from this tradition and denote explicit formulae, taking into account the non-ideal nature of the vapour phase.

For the case of a solution of a single electrolyte, converting mole fractions into molalities, in equation (12)

$$-\frac{1}{T}(L_1^\circ+\overline{H_1-H_1^\circ})\,dT+\bar{V}_1'\,dP=\frac{M_1m_2}{1000}\left(\frac{\delta\mu_2}{\delta m_2}\right)_{T,P}dm_2 \qquad \ldots\ (14)$$

where M_1 = molecular weight of the solvent and m_2 = molality of the solute.

Now, we have $\mu_2=\mu_2^\circ+RT\ln a_2=\mu_2^\circ+RT\ln m_2\gamma_2$,

where γ_2 is the activity coefficient referred to the molality scale ; hence

$$\left(\frac{\delta\mu_2}{\delta m_2}\right)_{T,P}=\frac{RT}{m_2}+RT\left(\frac{\delta\ln\gamma_2}{\delta m_2}\right)_{T,P} \qquad \ldots \qquad \ldots\ (15)$$

we define $\gamma_2 = \gamma_+^{\nu_+}\gamma_-^{\nu_-}$

where ν_+ and ν_- are the numbers of respective ions on dissociation.

The mean activity coefficient $\gamma_\pm$ is defined by

$$\gamma_\pm = (\gamma_+^{\nu_+}\gamma_-^{\nu_-})^{1/\nu}$$

so that $$\gamma_2 = \gamma_\pm^{\nu} \text{ and } \ln\gamma_2 = \nu \ln \gamma_\pm \quad \ldots \quad \ldots \quad (16)$$

Making use of (16), we have from equation (14)

$$+ \frac{1}{T}(L_1^\circ + \overline{H_1 - H_1^\circ})\, dT + \bar{V}_1'\, dP = \frac{RTM_1m_2}{1000}\left[\frac{1}{m_2} + \nu\left(\frac{\delta \ln\gamma_\pm}{\delta m_2}\right)\right] dm_2 \quad \ldots \quad (17)$$

we can substitute for $\ln \gamma_\pm$ either from the original Debye- Hückel equation or from the modifications of it proposed by several authors. We mention particularly the equation proposed by Stokes and Robinson, and Glueckauff which take into account the hydration of the ions. These equations have comparatively large ranges of validity (*i. e.* up to about $4m$) and hence can be safely used.

Solid-liquid-vapour Equilibrium

We can easily extend the formalism for studying solid-liquid-vapour equilibrium. In this connection we will consider the variation of vapour pressure of the solvent in a solution containing several electrolytes, kept saturated with the solid phase containing one electrolyte. The treatment will hold good for sparingly soluble electrolytes, so that the solution phase consists of only ions and solvent.

Using subscript 1 for the solvent and 2, 3 etc. for the ionic species, and using superscript (′) for the vapour phase, (″) for the solid phase and none for the liquid phase, we have for the component (1)

$$-(\bar{S}_1' - \bar{S}_1)\, dT + (\bar{V}_1' - \bar{V}_1)\, dP = -\left(\frac{\delta\mu_1}{\delta N_1}\right)_{T,P} dN_1 \quad \ldots \quad \ldots \quad (18)$$

Similary for the other ionic species, we have

$$-(\bar{S}_2'' - \bar{S}_2)\, dT = -\left(\frac{\delta\mu_2}{\delta N_2}\right)_{T,P} dN_2 \quad \ldots \quad \ldots \quad (19)$$

$$-(\bar{S}_3'' - \bar{S}_3)\, dT = -\left(\frac{\delta\mu_3}{\delta N_3}\right)_{T,P} dN_3 \quad \ldots \quad \ldots \quad (20)$$

and so on.

The term containing pressure does not appear in the above equation, since pressure is insignificant for solid-liquid equilibrium.

Multiplying equation (18) and equations (19), (20), by N_1, N_2, ... and adding and using Gibbs-Duhen relation for the vapour phase, we have

$$-\{N_1(\bar{S}_1' - \bar{S}_1) + N_2(\bar{S}_2'' - \bar{S}_2) + N_3(\bar{S}_3'' - \bar{S}_3) + \ldots\}\,dT$$

$$+ N_1(\bar{V}_1' - \bar{V}_1)\,dP = 0 \qquad \ldots \qquad \ldots \quad (21)$$

Putting $\bar{S}_1 - \bar{S}_1 = \dfrac{L_1^\circ + (H_1' - H_1^\circ)}{T}$ and $\bar{S}_2'' - \bar{S}_2 = -\dfrac{L_s}{T}$

where L_s is the heat of solution and neglecting $\bar{V}_1$, in comparison to $\bar{V}_1'$, we have from equation (21)

$$-\frac{1}{T}\{N_1L_1^\circ + N_1(H_1 - H_1^\circ) - N_2L_s\}\,dT + N_1\left(\frac{RT}{P} + B + C'P + \ldots\ldots\right)dP = 0 \quad \ldots \quad (22)$$

or

$$\frac{dP}{dT} = \frac{{}^1/_T\{N_1L_1^\circ + N_1(H_1 - H_1^\circ) - N_2L_s - \ldots\}}{N_1\left\{\dfrac{RT}{P} + B + C'P + \ldots\ldots\right\}} \qquad \ldots \quad (23)$$

In deducing the above equation we have assumed that only one electrolyte remains in the solid phase. L_s is the heat of solution of the said electrolyte. It need not be emphasised that the above formula strictly holds for solutions of sparingly soluble electrolytes

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MAGNETIC STUDY OF SOME METAL DERIVATIVES OF 1 : 3-β-DIKETONES. PART I

By Sagar Mehta and D. M. Desai

The diamagnetic susceptibilities of eleven metal acetylacetonates, namely, that of Be, Mg, Zn, Cd, Hg, Ca, Sr, Ba, Al, Zr and Th, have been studied. The results show the absence of singlet linkages in these compounds and appear to support the structure involving single and double bonds. The fair agreement between the observed and the calculated values of molar susceptibilities for all metal chelates except those of Zn, Cd and Hg suggests that there is no systematic and appreciable diamagnetic contribution due to the metal chelate bond in these compounds.

A study of the measurements of infra-red spectra (Duval, Freymann and Le Compte, *Bull. soc. chim.*, 1952, 106) and of the vibration spectra (Duval *et al.*, *Compt. rend.*, 1950, **231**, 272 ; Skoldinov and Shegorin, *Zur. Phiz. Chim.*, 1950, **24**, 955) of several metal derivatives of acetylacetone has led to the conclusion that these metal derivatives of acetylacetone exist only in the enolic form and that they are complexes, rather than salts. The metal derivatives of acetylacetone are therefore looked upon as chelate compounds. It appears from the literature that so far no systematic work has been done on the magnetic measurements of these metal chelates of acetylacetone.

Angus and Farquharson (*Proc. Roy. Soc.*, 1932, **136A**, 579) studied the diamagnetic susceptibility of the beryllium acetylacetone. The susceptibility of thorium acetylacetone was determined by Hutchisson and Elliott (*J. Chem. Phys.*, 1948, **16**, 920) with a view to ascertaining whether the chelated group had any diamagnetic correction to be applied in such compounds. In the present communication the diamagnetic susceptibility of several metal chelates of acetylacetone has been determined and the results discussed from the viewpoint of the structure of metal chelates. The diamagnetic contribution of the chelate group attached to the metal atom has also been examined.

Experimental

The metal chelates of acetylacetone, namely, Be, Mg, Zn, Cd, Hg, Ca, Sr, Ba, Al, Th and Zr acetylacetonates, were prepared by the known methods, using acetylacetone of Merck's quality and the inorganic salts of very high purity. Acetylacetone was twice distilled in a glass-joint apparatus before use. The compounds so prepared were carefully purified by repeated crystallisation and dried before measurement. The purity of the compounds was determined by m.p. and analysis of the metal content.

Diamagnetic Susceptibility Measurements.—The diamagnetic susceptibilities of these compounds were determined by a modified form of Gouy's balance (*Compt. rend.*, 1889, **109**, 935). Angus and Tilston (*Trans. Faraday Soc.*, 1947, **43**, 235) have recently obtained the usual equation for calculating the diamagnetic susceptibility in the following form :

$$\chi = \frac{\alpha F + C}{w} \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

where F = force on the specimen in mg., w = weight of the substance in g. and α and C are the constants; the value of $\alpha = 2l/(H_1^2 - H_2^2)$ and the value of $C = V \times k_m$, where k_m is the volume susceptibility of air (0.0294×10^{-6}). The equation (1) was used in the calculation of the diamagnetic susceptibility of the substances.

In order to determine the values of the constants α and C, a series of readings were taken with pure benzene (free from thiophene), since its susceptibility value ($\chi = -0.7023 \times 10^{-6}$) is known with accuracy (cf. Angus and Hill, *ibid.*, 1943, **39**, 185; Baddar, Hilal and Sugden, *J. Chem. Soc.*, 1949, 132). The average values of α and C found were 0.3425 and 0.0549 respectively.

The reliability of these values of α and C was checked by determining the susceptibility of pure KCl (found : -0.510×10^{-6}) and found in good agreement with the value (-0.516×10^{-6}) obtained by other workers.

The values obtained for the diamagnetic susceptibility of the metal acetylacetonates are shown in Table I (χ_s represents the specific susceptibility and χ_M, the molecular susceptibility). The susceptibility values are the mean of at least three different determinations. All the values of the susceptibilities have been expressed in terms of -1×10^{-6} C.G.S. units.

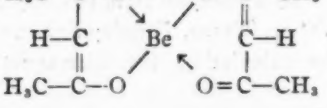
TABLE I

Acetyl-acetonates.	M.W.	χ_s.	χ_M.	χ_M (reported).	Acetyl-acetonates	M.W.	χ_s.	χ_M.	χ_M (reported).
Be	207.22	0.519	107.50	(107.90)*	Ca	238.29	0.475	113.20	
Mg	222.53	0.478	106.30		Sr	285.84	0.447	127.70	
Zn	281.61	0.432	121.60		Ba	335.57	0.390	130.90	
Cd	310.62	0.391	121.40		Al	324.29	0.466	151.10	
Hg	398.82	0.294	117.20		Zr	487.64	0.435	212.00	
					Th	628.54	0.372	233.70	(223.60) **

* Reported by Angus & Farquharson (*loc. cit.*).
** ,, Hutchisson *et al.* (*loc. cit.*).

From Table I the susceptibility value of Be acetylacetonate obtained by the authors appears to be in excellent agreement with that obtained by Angus and Farquharson (*loc. cit.*). The susceptibility value of Th acetylacetonate obtained by Hutchisson and Elliott is slightly lower than that obtained in this investigation.

Structure of Metal Chelates.—The metal chelates are usually represented by the structure which involves single and double bonds, as shown below for Be acetylacetonate.

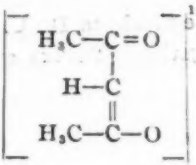


Sugden (*J. Chem. Soc.*, 1929, 318) from the measurements of parachor of acetylacetonate, propionylacetonate and basic acetate of Be has shown that these compounds

could only be represented by a structure involving singlet linkages. The existence of singlet linkages in normal and stable compounds is, however, highly improbable on quantum mechanical consideration, because a stable one-electron bond can be formed only when there are two conceivable electronic states of the system with essentially the same energy. The structure involving singlet linkages is therefore obviously ruled out.

The magnetic data obtained for these metal chelates (Table I) also indicate the absence of singlet linkages, as all the compounds are diamagnetic. If these metal chelates had single electron bonds, they would have shown an overwhelming paramagnetism due to unpaired electrons.

Calculation of χ of Acetylacetonate Ion.—The susceptibility of acetylacetonate ion has been calculated on the basis of the structure represented as above, by using Pascal's constants (Bhatnagar and Mathur, "Physical Principles and Application of Megneto-Chemistry", p. 94) for various atoms and constitutive correction factors. Accordingly, the structure of this ion is represented as



so that its susceptibility is given by

$$\chi = [5C] + [7H] + [-O-] + [=O] + \Sigma\lambda$$
$$= -30.0 - 20.51 - 4.61 + 1.73 + \Sigma\lambda$$
$$= -53.29 + \Sigma\lambda$$

where $\Sigma\lambda = 2\,C_3^{\alpha} + C_3^{\beta} + [C=C]$

$$= -2.58 - 0.48 + 5.50$$
$$= +2.44$$
$$= -50.95 \times 10^{-6}$$

Comparison of Molar Susceptibilities.—The observed molar susceptibilities of the metal chelates were compared with the values calculated by using the value of the acetylacetonate ion as computed above the and Angus values (*Proc. Roy. Soc.*, 1932, **136A**, 569) for various metal atoms. The observed and calculated values of molar susceptibilities χ_M are shown in Table II.

TABLE II

Acetyl acetonate.	χ_M		Acetyl acetonate.	χ_M		Acetyl acetonate.	χ_M	
	Obs.	Calc.		Obs.	Calc.		Obs.	Calc.
Be	107.50	102.25	Hg	117.20	149.47	Ba	130.90	133.49
Mg	106.30	104.79	Ca	113.20	112.32	Al	151.10	155.13
Zn	121.60	130.32	Sr	127.70	122.09	Zr	212.00	218.59
Cd	121.40	135.84				Th	233.70	229.70

Table II shows that for all the metal chelates, except those of Zn, Cd and Hg, the observed values of χ_M agree fairly well with the calculated ones ; slight differences are, of course, expected since the theoretical values used are for free ions. The fair agreement between the observed and calculated values of χ_M indicates that there is no systematic and appreciable diamagnetic contribution due to the metal chelate bond in these compounds. However, the differences observed in the case of Zn, Cd and Hg acetylacetonates are significant, and they are in the order of $8.72 < 14.44 < 32.77$. These results therefore suggest that at least in these metal chelates, there is an appreciable depression in diamagnetism due to the metal chelate bond which increases in the order: $Zn < Cd < Hg$.

It may be concluded therefore that for all metal chelates, except of Zn, Cd and Hg, there is no appreciable diamagnetic contribution due to the metal chelate bond. This is in agreement with the conclusion deduced by Hutchisson and Elliott from a study of thorium acetylacetonate.

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ON THE MECHANISM OF THE REACTION IN THE FORMATION OF THE BLUE PEROXYCHROMIC ACID

By Ram Chandra Rai

It has been found that the ethereal blue peroxychromic acid is not an acid but a chromium perchromate. The mechanism suggested is that due to the addition of H_2O_2 to $K_2Cr_2O_7$ solution, $Cr_2O_7^{2-}$ is oxidised to $Cr_2O_{10}^{2-}$ and simultaneously due to the presence of hydrogen ions, H_2O_2 reduces $Cr_2O_7^{2-}$ to Cr^{3+}, and this Cr^{3+} combines with $Cr_2O_{10}^{2-}$ to form chromium perchromate. In order to show the validity of this reaction, the blue peroxychromic acid has been prepared with $K_2Cr_2O_7$ solution, H_2O_2 and chromium sulphate solution without the presence of any acid.

Barreswil (*Compt. rend.*, 1848, **16**, 1085) observed that when an acidified solution of potassium dichromate was treated with hydrogen peroxide, 4 mols. of oxygen were given off per mol. of $K_2Cr_2O_7$, and he assumed that the peroxychromic acid, $Cr_2O_7H_2O$, was formed as an intermediate product. Aschoff (*J. prakt. Chem.*, 1860, **81**, 402; *Chem. News*, 1862, **5**, 129) represented the reaction as:

$$2CrO_3 + H_2O_2 \longrightarrow H_2O + Cr_2O_7,$$

followed by

$$Cr_2O_7 + 4H_2O_2 \longrightarrow Cr_2O_3 + 4H_2O + 4O_2.$$

Fairley (*J. Chem. Soc.*, 1877, **31**, 1, 125) assumed that the intermediate peroxychromic acid was $CrO_6 3H_2O$. Martinon (*Bull. soc. chim.*, 1886, *iii*, **45**, 862) regarded the peroxychromic acid as $4H_2O_2 2CrO_3$, *i. e.* H_4CrO_7 with an anhydride CrO_3. Carnot (*compt. rend.*, 1888, **107**, 948, 997) found the reaction of H_2O_2 on chromic acid to be a quantitative reduction of the acid. Berthelot (*compt. rend.*, 1889, **108**, 24, 157, 477) was of the opinion that two types of reactions took place when hydrogen peroxide was added to chromic acid, and when chromic acid was added to hydrogen peroxide. In the first case the reaction takes place as:

$$2CrO_3 + 3H_2O_2 + 3H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 3O_2 + 6H_2O$$

i.e., the chromic acid and hydrogen peroxide each loses the same quantity of oxygen. In the second case the reaction seems to occur in two stages:

$$2CrO_3 + H_2O_2 \rightarrow Cr_2O_7 + H_2O,$$

and then

$$Cr_2O_7 + 4H_2O_2 \rightarrow Cr_2O_3 + 4H_2O + 4O_2$$

when 1.66 times as much of oxygen is derived from the peroxide as from CrO_3. The intermediate Cr_2O_7 is considered to be the anhydride of the blue peroxychromic acid. Bauwann (*Z. angew. Chem.*, 1891, **4**, 135) confirmed the view of Berthelot.

A detailed study of the mechanism of the formation of the blue peroxychromic acid was made by Riesenfeld *et al.* (*Ber.*, 1905, **38**, 3380, 3578). According to him the reaction between CrO_3 and H_2O_2 takes place as:

$$2CrO_3 + 3H_2O_2 \rightarrow Cr_2O_3 + 3H_2O + 3O_2$$

with an intermidiate product Cr_2O_9 ; which may be represented as

$$2CrO_3 + 3H_2O_2 \rightarrow Cr_2O_9 + 3H_2O$$

followed by

$$Cr_2O_9 \rightarrow Cr_2O_3 + 3O_2,$$

and when the hydrogen peroixde is in excess:

$$2CrO_3 + 2H_2O_2 \longrightarrow 2CrO_4 + 2H_2O$$

followed by

$$2CrO_4 + 5H_2O_2 \longrightarrow Cr_2O_3 + 5H_2O + 5O_2$$

or else according to

$$2CrO_3 + 7H_2O_2 \longrightarrow Cr_2O_{13} + 7H_2O$$

followed by

$$Cr_2O_{13} \longrightarrow Cr_2O_3 + 5O_2.$$

Rai and Prakash have observed (*Z. anorg. Chem.*, 1954, **275**, 94) that the decomposition product of the ethereal blue peroxychromic acid is chromium dichromate. Further, it has been observed (Rai, this *Journal*, 1957, **34**, 68) that whether hydrogen peroxide is added to the chromic acid solution or *vice versa*, the same chemical substance is formed, and the ethereal blue peroxychromic acid after investigation has been found out to be chromium perchromate and not an acid, and the formula suggested is $Cr_2(Cr_2O_{10})_3$. It means that chromium is present not only in the form of perchromate ion but also as trivalent chromium in the ethereal blue peroxychromic acid. This view has been further confirmed (Rai, *loc. cit.*) that the complexes formed with pyridine and piperidine with ethereal blue peroxychromic acid contain trivalent chromium also.

In view of the above observations an attempt has been made to suggest the mechanism of the reaction in the formation of the blue peroxychromic acid when hydrogen peroxide is added to chromic acid solution. It is a well-known fact that chromic acid solution is a mixture of H_2CrO_4 and $H_2Cr_2O_7$, *i.e.*, it contains CrO_4^{2-} and $Cr_2O_7^{2-}$. When hydrogen peroxide is added to a solution of chromic acid or an acidified solution of $K_2Cr_2O_7$, $Cr_2O_7^{2-}$ ions are oxidised by H_2O_2 to $Cr_2O_{10}^{2-}$, which may be represented as

$$Cr_2O_7^{2-} + 3H_2O_2 \rightarrow Cr_2O_{10}^{2-} + 3H_2O$$

as well as H_2O_2 in the presence of hydrogen ions reduces $Cr_2O_7^{2-}$ ions to Cr^{3+}, which may be represented as

$$Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O.$$

Then the chromic ions, thus generated, react with the perchromate ions to afford chromium perchromate, which may be represented as:

$$2Cr^{3+} + 3Cr_2O_{10}^{2-} \longrightarrow Cr_2(Cr_2O_{10})_3.$$

This $Cr_2(Cr_2O_{10})_3$ is soluble in ether and therefore can be extracted with ether from the aqueous layer. Since there is also CrO_4^{2-} in chromic acid solution, there remains the possibility of formation of $Cr_2(CrO_4)_3$ due to the reaction between Cr^{3+} and CrO_4^{2-}. This fact has also been confirmed (cf. Rai this *Journal*, 1957, **34**, 59).

According to the mechanism of reaction suggested in the formation of the ethereal blue peroxychromic acid, a very interesting point arises, viz., if to an aqueous solution of $K_2Cr_2O_7$ hydrogen peroxide is added, then $Cr_2O_7^{2-}$ will be oxidised to $Cr_2O_{10}^{2-}$, and

now if to this mixture an aqueous chromic salt solution is added, the chromic ions and the perchromate ions should react to furnish the blue peroxychromic acid (the chromium perchromate) which may be extracted with ether from the aqueous layer. This mode of reaction in the formation of the blue peroxychromic acid has been experimentally observed, as when to an aqueous solution of $K_2Cr_2O_7$ hydrogen peroxide is added and then to this mixture a chromic sulphate solution is added, the blue peroxychromic acid is formed which is extracted with ether ; its nature has been experimentally investigated.

EXPERIMENTAL

A 5% solution of $K_2Cr_2O_7$ (25 c.c.) was cooled in ice and to this 10 c.c. of ice-cooled 20 vol. of H_2O_2 was added when a black substance was formed. To this mixture various amounts of 5% chromic sulphate solution were added and the blue compound that formed was extracted with 50 c.c. of ice-cooled ether and separated from the aqueous layer in a separating funnel. A portion of the ethereal layer (10 c.c.) was taken in a tared silica crucible, evaporated to dryness on a water-bath, ignited and weighed. The weight represents the weight of Cr_2O_3. Another portion (10 c.c.) from the same solution was taken in a flask and left for decomposition and then titrated iodimetrically against a standard hypo solution. A third 10 c.c. portion from the ethereal solution was titrated in two stages against the same hypo solution : first without any acid and then in the second stage with 5 c.c. of $2N$-H_2SO_4 solution. The observations are recorded in Table I.

TABLE I

5% $K_2Cr_2O_7$ soln. taken = 25 c.c.
20 Vol. H_2O_2 taken = 10 c.c. Ether taken = 50 c.c.

Vol. of 5% chromic sulphate soln. added.	Cr_2O_3 present in 10 c.c. of blue perchromate.	Volume of hypo used in titrating			c+d/b.	c+d/e.	d/e.	c/d.
		first stage	2nd stage	10 c.c. of decomp. product.				
a.	b.	c.	d.	e.	f.	g.	h.	i.
5 c.c.	0.0032 g.	2.40 c.c.	3.80 c c.	3.03 c.c.	1937	2.06	1.26	0.63
10	0.0052	3.80	6.10	4.90	1903	2.02	1.22	0.62
15	0 0094	6.10	9.00	7.50	1607	2.01	1 20	0 67
20	0 0102	7.30	11.40	9.30	1833	2.01	1.22	0.64
25	0 0128	9.30	13.80	11.30	1804	2.05	1 22	0.67
30	0.0126	8.80	13 40	10.90	1761	2.01	1.21	0.68

It is quite clear from the above table that all the ratios shown there are similar to those shown earlier (Rai, *loc. cit* , p. 59). Therefore it may be easily concluded that the blue peroxychromic acid prepared by either chromic acid solution and the acidified solution of $K_2Cr_2O_7$ and H_2O_2, or an aqueous solution of $K_2Cr_2O_7$, H_2O_2 and chromic sulphate appears to be the same as all their chemical and physical properties are similar in all respects. Therefore it may be assumed that the formation of the blue peroxychromic acid may be due to the $Cr_2O_{10}^{2-}$ and the chromic ions generated due to the simultaneous oxidation-reduction of $Cr_2O_7^{2-}$ with H_2O_2. We may therefore safely assume this compound to be chromium perchromate.

Arguments can be adduced that the formation of the blue peroxychromic acid may be due to the acid generated by the hydrolysis of chromic sulphate and not by the chromic ions from $Cr_2(SO_4)_3$. In order to make this point clear, the *p*H of the chromic sulphate solution was measured by a *p*H-meter ; a sulphuric acid solution of the same *p*H was prepared and parallel experiments were done with H_2SO_4 of the same *p*H as of chromic sulphate solution. The *p*H of the chromic sulphate was found to be 2.5 and so H_2SO_4 of *p*H 2.5 was prepared and the blue peroxychromic acid was prepared with $K_2Cr_2O_7$ solution, H_2O_2 and H_2SO_4 of *p*H 2.5. The results are shown in Table II.

TABLE II

Volumes of the materials taken are the same as in Table I.

H_2SO_4 of *p*H 2.5 taken.	Cr_2O_3 obtained from 10 c.c. of the ethereal blue compound.	Hypo used in the titration of 10 c.c. of the blue compound.
Nil	0.0007 g.	2.1 c.c.
20 c.c.	0.0012	3.0
25	0.0022	4.2
30	0.0018	3.8

It is quite clear from the above table that the concentrations of peroxychromic acid formed with H_2SO_4 solution of *p*H 2.5 are very much lower than the corresponding values of peroxychromic acid formed with chromic sulphate using the same volumes of H_2SO_4 and $Cr_2(SO_4)_3$ solutions under the identical conditions. It is of interest to see that even in the case of aqueous solution of $K_2Cr_2O_7$ without any acid, a small concentration of peroxychromic acid is formed. This is due to the slight acidity of $K_2Cr_2O_7$ solution. It is thus concluded that the blue peroxychromic acid of the concentration shown in Table I cannot be due to the hydrolysis of chromic sulphate solution, but is due to the chromic ions in the chromic sulphate solution. The weight of Cr_2O_3 in the two tables can also suggest the same thing.

It is of interest to note that in the formation of this blue perchromate, when to aqueous solutions of $K_2Cr_2O_7$ and K_2CrO_4, H_2O_2 is added separately, black compounds are formed in both the cases. But when to both the above mixtures chromic sulphate solution is added separately, the blue compound is formed only in the case of dichromate solution. The above fact shows that probably the formation of the perchromate ion is due to the oxidation of $Cr_2O_7^{2-}$ and not to CrO_4^{2-}. For what has been observed, the blue ethereal compound appears to be $Cr_2(Cr_2O_{10})_3$.

From this mode of formation of the chromium perchromate, it appears that by taking potassium dichromate, H_2O_2 and solutions of other cations, diverse perchromates may be prepared ; but successful application of this method in the case of other per chromate depends on their separation from the aqueous layer.

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STUDIES IN COMPLEX FORMATION WITH COLLOIDAL MERCURI-SULPHOSALICYLIC ACID. PART I. COMPLEX BERYLLIUM MERCURI-SULPHOSALICYLATE

By Rajendra S. Singh and Satya Prakash

Mercuri-sulphosalicylic acid forms complexes with metal ions similar to those obtained with sulphosalicylic acid, as it possesses the same co-ordinating groups. Potentiometric and conductometric studies reveal that mercuri-sulphosalicylic acid forms two types of complexes with beryllium: (*i*) 1 : 1 complex in acidic medium and (*ii*) 1 : 2 complex in alkaline medium. Both the complexes are very stable as the beryllium is not precipitated from the complex even in highly alkaline solutions. In both the complexes, the phenolic hydrogen is displaced during complex formation.

The mercury compounds of sulphophenol carboxylic acid and their homologues (Saccharin, Fabrik Aktien-Gesellschaft vorm. Fahlberg List and Co., *British Chem. Abs.*, 1920, 673), when dispersed in water, yield colloidal solutions. Ostwald (*Koll.-Chem. Beih.*, 1926, **23**, 242) investigated the colloidal nature of complex mercury derivatives of sulphosalicylic acid. As mercury forms a compound of structure $C_6H_4-COOH-HgOH$ with benzoic acid and a compound of structure $C_6H_3-OH-COOH-HgOH$ with salicylic acid, Ostwald has assigned the structure of mercuri-sulphosalicylic acid as $HO_3S-C_6H_2-OH-COOH-HgOH$. Since this compound possesses the same co-ordinating groups as sulphosalicylic acid, it forms complexes similar to those obtained with the latter.

Experimental

Colloidal Mercuri-sulphosalicylic Acid.—From a solution of mercuric chloride (A.R., B.D.H.) mercuric oxide was precipitated by the addition of an excess of NaOH solution, and the precipitate thoroughly washed with distilled water till free of hydroxyl and chloride ions. The precipitate was dissolved in a concentrated solution of sulphosalicylic acid (G.R., E. Merck), the ratio of the oxide to acid being 1 : 2. The white gel, obtained on drying over a water-bath, furnished a greyish solid, which was washed with alcohol to free it of excess of unchanged sulphosalicylic acid. The powder obtained on drying was white and hygroscopic. This, when dissolved in water, gave a clear transparent colloidal solution. Solutions of requisite strength were prepared by dissolving a known amount of the powder and finally standardised by titration against a standard alkali solution. Due to the high viscosity of the colloidal solution, solutions of concentrations above 0.07*M* could not be prepared at room temperatures (below 30°). The mercury of the colloid was estimated gravimetrically as HgS. The ratio of mercury to sulphosalicylic acid in the compound was found 1 : 1, thus confirming Ostwald's formula of colloidal mercuri-sulphosalicylic acid.

In the study of the complex formation with mercuri-sulphosalicylic acid and beryllium ions, it was not possible to use the colloidal solution, as coagulation occurred due to the free electrolyte present. Hence, potassium chloromercuri-sulphosalicylate, obtained by the addition of an excess of potassium chloride to the colloid, was used in place of mercuri-sulphosalicylate. A solution of this compound in water behaves like a true solution. The monosodium salt of this compound was obtained by neutralisation with a calculated volume of a standard alkali solution.

Standard solutions of beryllium sulphate were prepared by direct weighing of A.R., B.D.H. $BeSO_4,4H_2O$ and dissolution in water. Fresh solutions have been employed, as stocked solutions are known to undergo hydrolysis.

All measurements were done at a constant temperature of $32° \pm 0.1°$. The electrical conductivity was measured with Leeds Northrup's Kohlrausch Slidewire, with an audiofrequency oscillator in the circuit. The conductivity cell was one with cell constant of 0.1400, and the point of balance detected by a headphone.

The p_H measurements were made with Leeds Northrup's A.C.-operated p_H-meter, using glass and saturated calomel electrodes. The instrument was calibrated with a standard buffer solution, and gave readings accurate to 0.02 units over the p_H scale.

Complex-forming Systems

In the study of complex formation of beryllium (II) with potassium chloromercuri-sulphosalicylate and its monosodium salt, the monovariant method was used. To a constant volume of beryllium sulphate solution were added varying amounts of complexing agent, keeping the total volume constant. Thus, a number of mixtures containing beryllium sulphate and the complexing agent in the ratios of 1 : 1, 1 : 2 and 1 : 4 were prepared. These mixtures were then titrated against a standard caustic soda solution. A known volume of the mixture was taken and to it varying quantities of alkali solutions were added, keeping the volume constant. The mixtures were left in a thermostat to attain equilibrium, after which the specific conductivity and p_H measurements were made. For comparison, the specific conductivity and p_H studies were made also separately with beryllium sulphate and potassium chloromercuri-sulphosalicylate solutions, when titrated with alkali under similar conditions.

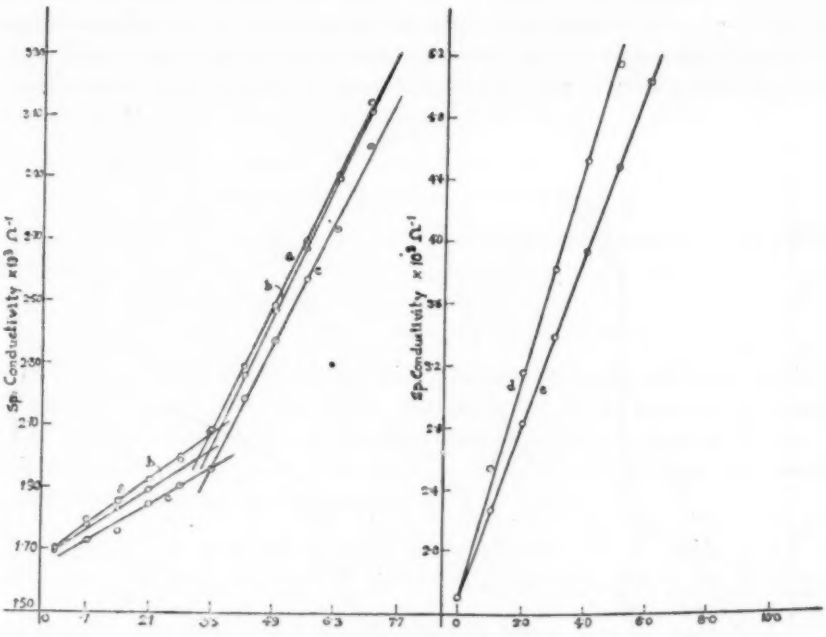
The typical reproducible results obtained out of a large number of experiments performed are shown in Figs. 1-5.

Discussion

Before investigating the complex formation between beryllium and mercuri-sulphosalicylic acid, it was thought to be of interest to make some observations on the nature of colloidal mercuri-sulphosalicylic acid. The effects of potassium chloride, potassium bromide, potassium thiocyanate, potassium nitrate and potassium sulphate on the colloidal nature of mercuri-sulphosalicylic acid have been studied. The results are graphically represented in Fig. 1, where curves a,b,c,d and e represent the changes

n the specific conductivity of mercuri-sulphosalicylic acid with the progressive addition of KCl, KBr, KCNS, K_2SO_4 and KNO_3 respectively. Curves d and e show a

FIG. 1



continuous rise in the conductivity of the system with increasing concentration of the electrolyte added, while curves a, b, and c show a sharp discontinuity. The concentration of mercury in mercuri-sulphosalicylic acid in g. ion per litre of the solution is 6.739×10^{-3} and the concentration of KCl, KBr and KCNS at the point of discontinuity, in g. ion per litre of the solution is 6.860×10^{-3}. It is interesting to note that at the break of the curve, the concentration of the electrolyte is nearly equal to the concentration of mercury in the colloid. It shows that one mole of mercuri-sulphosalicylic acid takes up only one mole of KCl, KBr or KCNS to form a compound of the type potassium chloromercuri-sulphosalicylate (with KCl). The reaction may be represented as:

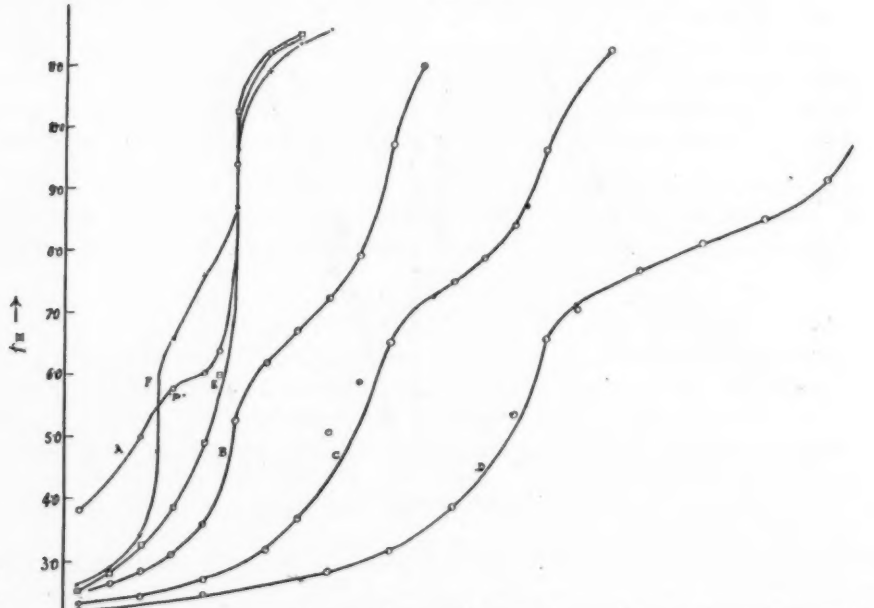
$$\left.\begin{array}{l} HO_3S-C_6H_3-OH-COOH + HgO \rightarrow HO_3S-C_6H_2-OH-COOH-HgOH \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \overset{KCl}{\downarrow} \qquad\qquad \ldots \qquad\qquad \ldots \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad KO_3S-C_6H_2-OH-COOH-HgCl \end{array}\right\} \quad (I)$$

The potassium chloride compound possesses no colloidal properties, and affords shining, white, fibrous precipitate from a concentrated solution. This precipitate is soluble in water and behaves like a true solution.

It has been shown by Ostwald (*loc. cit.*) and Thiele (*Kolloid Z.*, 1952, **127**, 134) that the effect of Cl^-, Br^- and CNS^- on mercuri-sulphosalicylic acid is a case of true chemical combination, as equivalent amounts of the reactants are required. The reaction has been represented as (I).

Fig. 2 represents the changes in the p_H that take place when beryllium sulphate, potassium chloromercuri-sulphosalicylate and their mixtures in different proportions are titrated with alkali respectively. The abscissa represents the number of equivalents (*a*) of alkali added per gram ion of hydrogen of the mercuri-sulphosalicylic acid.

FIG. 2



Equivs. of alkali added (a).

Curves A to D are for solutions that are $6.25 \times 10^{-3}M$ in beryllium sulphate with no added potassium chloromercuri-sulphosalicylate and with 1, 2 and 4 equivalents added respectively. Curves E and F are for $6.25 \times 10^{-3}M$ solutions of mercuri-sulphosalicylic acid and potassium chloromercuri-sulphosalicylate.

From the graph it can be seen that the addition of hydroxyl ions to beryllium sulphate does not cause immediate precipitation. Over one equivalent of alkali has to be added before precipitation starts, and is complete when two equivalents have been added. This has also been reported by Britton (*J. Chem. Soc.*, 1925, **127**, 2121). The reaction may be represented as:

$$BeSO_4 + 2\,NaOH \longrightarrow Be(OH)_2 + Na_2SO_4 \quad \ldots \quad \ldots \quad (1)$$

The neutralisation of mercuri-sulphosalicylic acid (Fig. 2, curve F) shows one sharp inflexion at $a=2$, which indicates that the colloid behaves like a dibasic acid.

$$HO_3S - C_6H_2 - OH - COOH - HgOH + 2NaOH \longrightarrow NaO_3S - C_6H_2 - OH - COONa - HgOH \quad \ldots \quad (2)$$

The phenolic hydrogen does not ionise even at high values of p_H.

Potasssum chloromercuri-sulphosalicylate (curve E) shows two definite inflexions, one at $a=1$ and the other at $a=2$. The first inflexion occurs at p_H range 3.50–6.50, indicating the ionisation of the carboxyl hydrogen only.

$$KO_3S - C_6H_2 - OH - COOH - HgCl + NaOH \longrightarrow KO_3S - C_6H_2 - OH - COONa - HgCl \quad \ldots \quad (3)$$

The second inflexion at the p_H range 8.0–11.0 indicates the ionisation of the phenolic hydrogen also.

$$KO_3S - C_6H_2 - OH - COONa - HgCl + NaOH \longrightarrow KO_3S - C_6H_2 - ONa - COONa - HgCl \quad \ldots \quad (4)$$

With one equivalent of potassium chloromercuri-sulphosalicylate added to beryllium sulphate (curve B) no decrease in the initial p_H of the mixture is observed, but there is an inflexion at $a=2$. The beryllium of the complex formed is not precipitated even at high values of p_H (10.0), which shows the stability of the complex. The reaction may be represented by equation as:

$$KO_3S - C_6H_2 - OH - COOH - HgCl + Be^{2+} \longrightarrow [(O_3S - C_6H_2 - O - COO - HgCl)Be]^- + 2H^+ + K^+ \quad \ldots \quad (5)$$

This suggests that the phenolic hydrogen is displaced during complex formation.

With 2 and 4 equivalents of potassium chloromercuri-sulphosalicylate added to beryllium sulphate (Fig. 2, curves C and D), the behaviour is different. Curve C shows an inflexion at $a=4$ and curve D at $a=6$, respectively. This indicates that a mol. of beryllium co-ordinates with two potassium chloromercuri-sulphosalicytate mols. to form an 1:2 complex. This complex also is very stable, as the beryllium is not precipitated. The reaction may be represented as:

$$2(KO_3S - C_6H_2 - OH - COOH - HgCl) + Be^{2+} \longrightarrow [(O_3S - C_6H_2 - O - COO - HgCl)_2.Be]^{4-} + 4H^+ + 2K^+ \quad \ldots \quad (6)$$

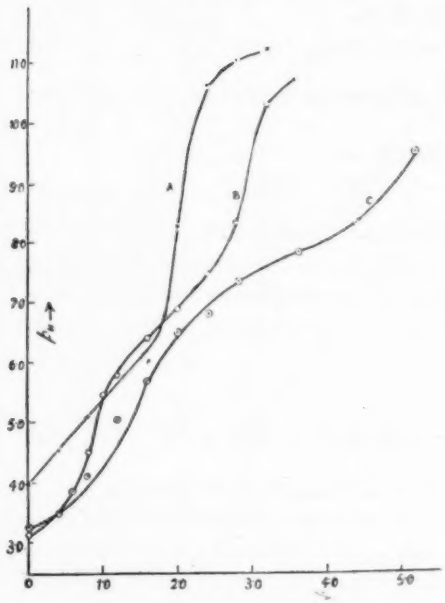
The excess of potassium chloromercuri-sulphosalicylate remains ionised in solution.

Fig. 3 represents the changes in p_H when solutions, that are $3.125 \times 10^{-3}M$ in (*i*) beryllium sulphate (curve A), (*ii*) 1:1 and 1:4 mixtures of beryllium with monosodium potassium chloromercuri-sulphosalicylate (curves B & C) are titrated with alkali respectively. The abscissa represents the number of equivalents of alkali added (*a*) The addition of alkali to beryllium sulphate has already been discussed (vide equation 1). The 1:1 mixture of beryllium ion and monosodium potassium chloromercuri-sulphosalicylate (curve B) has an initial p_H (3.10) which is lower than both that of beryllium sulphate (3.95) or the monosodium salt (6.10) alone, showing an

increase in the hydrogen-ion concentration of the mixture. There is an inflexion in the p_H curve at $a=1$, and the beryllium of the complex formed is not precipitated even in alkaline solution. This indicates clearly that the phenolic hydrogen is displaced during complex formation, according to the equation :

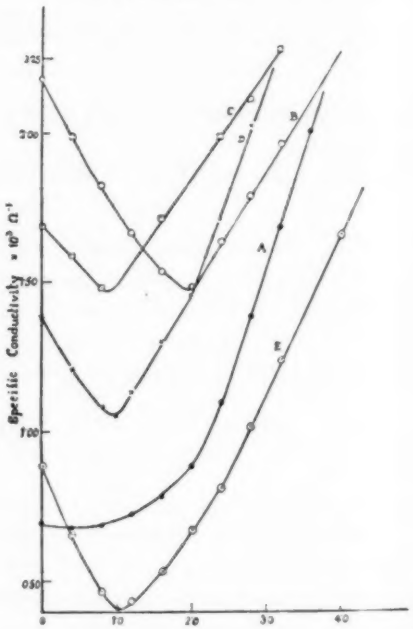
$$KO_3S - C_6H_3 - OH - COONa - HgCl + Be^{2+} \longrightarrow$$
$$[(O_3S-C_6H_3-O-COO-HgCl)\,Be]^- + H^+ + K^+ + Na^+ \quad \ldots \quad (7)$$

FIG. 3



Equivs. of alkali added (a).

FIG. 4



Equivs. of alkali added (a).

With 1 : 4 mixture (curve C) the behaviour is different. The initial p_H of the mixture is lower than that of the beryllium sulphate and monosodium salt alone, but the inflexion occurs at $a=2$. This indicates that the complex formed contains beryllium ion and the monosodium salt in the ratio of 1 : 2. The beryllium of the complex is not precipitated even in alkaline solutions. The reaction may be represented as :

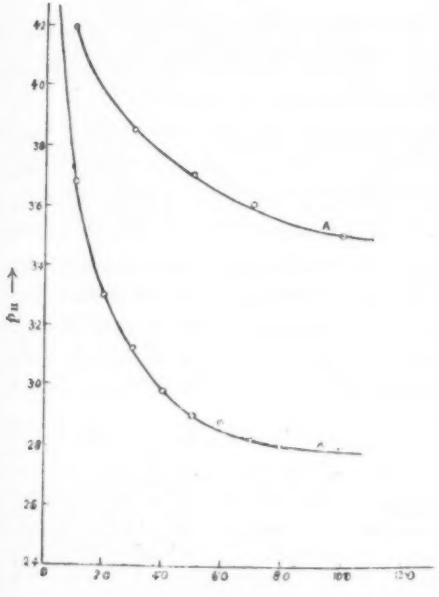
$$2(KO_3S - C_6H_3 - OH - COO - HgCl) + Be^{2+} \longrightarrow$$
$$[(O_3S-C_6H_3-O-COO-HgCl)_2Be]^{4-} + 2H^+ + 2K^+ + 2Na^+ \quad \ldots \quad (8)$$

Fig. 4 represents the changes in the specific conductivity when solutions, that are $3.125 \times 10^{-3}M$ in (*i*) beryllium sulphate (curve A), (*ii*) 1 : 1 mixtures of beryllium with potassium chloromercuri-sulphosalicylate (curve B) and its monosodium salt (curve C) respectively, (*iii*) potassium chloromercuri-sulphosalicylate (curve D), and

(*iv*) mercuri-sulphosalicylic acid (curve E), are titrated with alkali respectively. The abscissa represents the number of equivalents of alkali added (*a*). The neutralisation of potassium chloromercuri-sulphosalicylate (curve D) shows a minima at $a=1$ and discontinuity in the graph at $a=2$, according to equations (3) and (4). The neutralisation of mercuri-sulphosalicylic acid (curve E) also shows a minima at $a=1$ and a discontinuity at $a=2$, whereas the p_H curve (Fig. 2, curve E) shows only one inflexion at $a=2$, according to equation (2). It seems probable that the minima is due to the replacement of sulphonic hydrogen by sodium, as it is more acidic than the carboxyl hydrogen.

The addition of alkali to beryllium sulphate (curve A) produces little change in the conductivity values in the beginning, but it increases sharply after the addition of two equivalents of alkali ($a=2$); the reaction may therefore be represented by equation (1).

FIG. 5



$BeSO_4$ *added in c c.*

The addition of alkali to 1 : 1 mixtures of beryllium ions with potassium chloromercuri-sulphosalicylate and its monosodium salt (Fig. 4, curves B and C) shows minima at $a=2$ and $a=1$, respectively. The solutions behave as if it were of a dibasic and monobasic acids (vide equations 5 and 7). This gives clear evidence that a complex is being formed and that the phenolic hydrogen is displaced during complexation. The co-ordination takes place between the oxygen atoms of carboxyl and sulphonic groups.

Fig. 5 represents the p_H changes that take place when beryllium sulphate is added to monosodium potassium chloromercuri-sulphosalicylate. Curve A represents the p_H of the mixture solutions while curve A′ represents the p_H of beryllium sulphate alone. The p_H of the monosodium salt decreases with the addition of beryllium and becomes nearly constant when one equivalent has been added. As the mixture curve A lies below the beryllium sulphate curve A′, it shows that there is an increase in the hydrogen ion concentration which can only be explained due to the displacement of phenolic hydrogen during complex-formation (vide equation 7).

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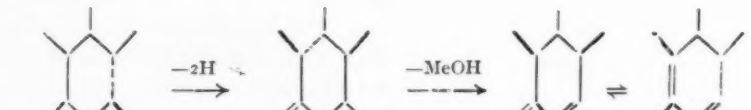
DEGRADATION OF ACONITINE

By Sharda Dasgupta and Bhola Nath

On oxidation with aluminium *tert.*-butoxide, aconitine yields a product, aconitinone. The latter on heating produces a methoxyl-free compound, designated as aconitoline, which has been shown to be an $\alpha\beta$-unsaturated ketone from its U. V. and I. R. spectra. An infra-red absorption spectrum of pyroaconitine reveals that pyrolysis of aconitine proceeds through the formation of an ethylenic linkage and not an epoxy group. Pyrolytic products obtained at a higher temperature are also described.

This communication outlines the results of a study of the oxidation of aconitine with aluminium *tert.*-butoxide and its pyrolysis at different temperatures, the principal aim of which is to establish the mechanisms of these reactions.

In aconitine, $C_{34}H_{47}O_{11}N$, aluminium *tert.*-butoxide specifically oxidises one secondary hydroxyl to a carbonyl group. The resulting product, aconitinone ($C_{34}H_{45}O_{11}N$), on heating readily splits off a molecule of methanol, yielding a base, aconitoline, $C_{33}H_{41}O_{10}N$. The latter contains in its ultraviolet absorption curve maxima at 232 mμ (log ϵ 4.1) and 274 mμ (log ϵ 2.83) which are characteristics of an $\alpha\beta$-unsaturated ketone (Gillman and Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry", Edward Arnold Publishers, London, 1954, p. 90), and thus confirm the following mode of reaction proposed by Majima and Tamura (*Annalen*, 1940, **545**, 1). The latter was also prepared from aconitine by its oxidation with chromic acid.



Aconitine. Aconitinone. Aconitoline.

The presence of an $\alpha\beta$-unsaturated ketone in aconitoline is further confirmed by the fact that its infra-red spectrum exhibits a strong band at 5.97μ.

On pyrolysis just above the melting point (205°), aconitine loses one molecule of acetic acid, furnishing pyroaconitine, $C_{32}H_{43}O_9N$. The mechanism by which this reaction takes place has not been settled (Manske and Holmes, 'The Alkaloids', Vol. IV, 1954, pp. 296-299). Pyroaconitine has been assumed to contain either an epoxy group, created by elimination of acetic acid between the acetoxy group and an adjacent hydroxyl (Dunstan and Carr, *J. Chem. Soc.*, 1894, **65**, 178; Schulze and Liebner, *Arch. Pharm.*, 1913, **251**, 453; 1916, **254**, 567) or an ethylenic linkage analogous to pyro-α-oxodelphinine (Jacobs and Huebner, *J. Biol. Chem.*, 1947, **170**, 209).

However, infra-red spectroscopy offers a very promising approach towards the clarification of this mechanism. Absorption spectrum of aconitine (Nath, this *Journal*, 1955, **32**, 25) contains a strong band at 6.02μ due to a non-conjugated double bond. But pyroaconitine does not exhibit in its absorption curve any band at 6.02μ, but instead a doublet near 6.22-6.33μ, showing definite diene conjugation. This could only arise if a new ethylenic linkage is introduced in the conjugated position to that initially present during pyrolysis by abstraction of a molecule of acetic acid between the ester grouping and a hydrogen atom from a neighbouring carbon atom. Thus, the mode of elimination of acetic acid is through an olefinic linking and not *via* an epoxide. This conclusion has been supported by catalytic hydrogenation experiment of pyroaconitine when it shows an uptake of approximately 5 moles of hydrogen, 3 moles due to benzoyl group and two moles due to two C=C bonds.

It is of interest to record that when pyrolysis of aconitine is effected at 250-60°/2 mm, the elimination of acetic acid is followed by deposition of :

(*i*) A colorless sublimate (A) consisting of needles, $C_7H_6O_2$, m.p. 122-24°. It does not contain nitrogen. It is acidic in character. Its ultraviolet absorption curve has a maximum at 228 mμ (log ϵ 4.08) and an inflexion at 272 mμ (log ϵ 3.06). The infra-red absorption spectrum possesses bands at 3.78 μ, 5.98 μ, 7.60μ, 7.84 μ and 10.78 μ, probably due to an acid.

(*ii*) A pale yellow resin (B), m.p. 108-110°. Its U. V. absorption spectrum has a maximum at 230 mμ (log ϵ 3.96) and infra-red curve contains, besides many common bands with the parent substance, aconitine, some bands at 6.39 μ and 6.48 μ.

Experimental

Infra-red Absorption Spectra.—The data recorded were obtained with a Grubb-Parsons single-beam absorption spectrophotometer having a sodium chloride prism. All the above substances were examined in a solution of known concentration in purified CCl_4 in the region 2.8 μ to 7 μ and in CS_2 in the region 7 μ to 15 μ in a rock salt cell having a capacity of 0.1 c.c.

Oxidation of Aconitine : (*a*) *With* Al-tert.-*butoxide.*—A mixture of aconitine (0.5 g.), aluminium *tert.*-butoxide (1.5 g.), dry *cyclo*hexanone (20 c.c.) and dry toluene (70 c.c.) was refluxed for 6 hours. After cooling, the suspension was extracted with 10% H_2SO_4. The acid extract was washed several times with ether to remove *cyclo*hexanone and then treated with an excess of 20% NaOH solution and extracted with ether ; the ethereal extract was dried (anhydrous Na_2SO_4) and the solvent removed when a slightly pink residue was obtained. This was crystallised from ethyl acetate, m. p. 148-49°. (Found : C, 63.4 ; H, 6.7. Calc. for $C_{34}H_{45}O_{11}N$: C, 63.5 ; H, 7.0%).

The above product aconitinone (0.1 g.) was dissolved in methanol (10 c.c.) and the solution refluxed for 1 hour. After reducing the volume to one third, it was chilled when a small quantity of a flocculent precipitate separated, m.p. 220°. (Found : C, 64.5 ; H, 7.3. Calc. for $C_{33}H_{41}O_{10}N$: C, 64.9 ; H, 6.8%).

(*b*) *With Chromic Acid.*—Aconitine (1.5 g.) was dissolved in acetone (90 c.c.) and cooled in an ice-salt mixture. To this was added a cooled solution of chromic anhydride (1.5 g.) and water (0.75 g.) in acetone (15 c.c.). After keeping the mixture at 15° for 10 days the solvent was removed in vacuo, the residue disssolved in sulphurous acid and extracted with ether. The aqueous layer was made alkaline with sodium carbonate and the precipitated base collected. This was crystallised from ethyl acetate, m.p. 149-50° and its mixed m.p. with the above aconitinone, 149-50°, was undepressed.

Pyrolysis of Aconitine.—Aconitine (0.2 g.) was heated as 203-205°/2 mm for 1 hour and the residue (pyroaconitine) crystallised from a mixture of ether and light petroleum, m. p. 169-70°. (Found : C, 65.8 ; H, 6.9. Calc. for $C_{32}H_{43}O_9N$: C, 65.6; H, 7.3%).

Hydrogenation.—Pyroaconitine (15.4 mg.) was hydrogenated with platinum oxide catalyst (30 mg.) in ethanol containing a drop of HCl. The process was completed in 2 hours with an absorption of hydrogen (found : 2.8 c.c., calc. ~ 4.6 moles). After removing the catalyst and the solvent, the product was crystallised from ethanol, m. p. 162°. (Found : C, 64.9 ; H, 8.5. Calc. for $C_{32}H_{53}O_9N$: C, 64.5 ; H, 8.9%).

In another experiment aconitine (1.1 g.) was first heated at 205°/2 mm and after an hour the temperature was raised to 250-260°/2 mm, furnishing (A) and (B).

(*A*) : A colorless sublimate in the form of needles, m.p. 122-24°. [Found : C, 68.9 ; H, 4.86 ; M.W. 130 (Rast). $C_7H_6O_2$ requires C, 68.8 ; H, 4.9%. M.W. 122].

(*B*) : A pale yellow resin, m. p. 108-10°, also sublimed and its composition was found to be C, 63.95 ; H, 7.5 ; N, 2.9%. It could not be induced to crystallise from any solvent.

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COMPLEX COMPOUNDS OF BIPOSITIVE SILVER WITH PYRIDINE CARBOXYLIC ACIDS. PART II. ARGENTIC COMPOUNDS OF PYRIDINE DICARBOXYLIC ACIDS

By Bireswar Banerjee and Priyadaranjan Rây

In continuation of our previous work on bipositive silver complexes of pyridine monocarboxylic acids, we have now been able to prepare the argentic complexes of all the dicarboxylic acids of pyridine with the exception of that of dinicotinic acid, which is not at hand for the present.

Argentic complexes of quinolinic, cinchomeronic, *iso*cinchomeronic, lutidinic and dipicolinic acids are formed by the oxidation of silver nitrate in presence of the corresponding acid by alkali persulphate in aqueous medium. They form red to dark red, finely divided crystals, more or less sparingly soluble in water. The argentic complex of dipicolinic acid has, however, been obtained in two different colours – dark red and green, the last one being produced at a lower temperature. The composition of all these complexes is given by the general formula $Ag^{II}(XH)_2$ (where XH_2=one molecule of the pyridine dicarboxylic acid). With the exception of cinchomeronic acid (3 : 4), all the complexes may be represented by a monomeric structure like that of the argentic picolinate. The structure of the argentic cinchomeronate resembles possibly that of nicotinic or *iso*nicotinic acid, being either dimeric, or polymeric with the formation of unending two-dimensional sheets and layers. The complexes are all decomposed by acids and alkalies.

All these argentic complexes are paramagnetic and give moment values of approximately 1.73 μ_B. X-ray powder photographs show that the green and chocolate modifications of the argentic complex of dipicolinic acid differ in their crystal structure. Cupric and argentic quinolinates crystallise with different water molecules and hence show, as might be expected, different X-ray patterns.

In a previous paper (this *Journal*, 1956, **33**, 503) an account of the preparation, properties and constitution of the argentic complexes of pyridine monocarboxylic acids, like nicotinic and *iso*nicotinic acids, has been given, which, with the argentic picolinate previously described by Barbieri (*Atti Accad. Lincei*, 1933, **17**, 1078), show that all the three pyridine monocarboxylic acids (α, β and γ) are capable of forming chelate inner-metallic complexes with bipositive silver. It has now been observed that pyridine dicarboxylic acids also behave in a similar manner. Of the six different pyridine dicarboxylic acids, argentic complexes with five of these, viz., quinolinic (2 : 3), cinchomeronic (3 : 4), *iso*cinchomeronic (2 : 5), lutidinic (2 : 4) and dipicolinic (2 : 6) acids, have been prepared for the present. It has, however, not yet been possible to obtain the remaining 3 : 5-dicarboxylic acid of pyridine (dinicotinic acid) in sufficient quantities to investigate the formation of its argentic complex.

The argentic complexes of all the above pyridine dicarboxylic acids are formed by the oxidation of silver nitrate in the presence of the acid concerned by means of sodium or potassium persulphate in aqueous medium in the cold. All the complexes excepting that of 2 : 6-acid (dipicolinic acid) form red to dark red crystalline products ; while the latter gives rise to two different coloured forms, green and dark chocolate. Their composition is represented by the general formula, $Ag^{II}(XH)_2$ (where XH_2 = one molecule of the dicarboxylic acid). One of the -COOH groups of each ligand molecule

remains obviously free in the complex. All the complexes, with the exception of that of cinchomeronic acid (3 : 4), are possibly represented by a monomeric structure like that of argentic picolinate. The structure of the argentic complex of cinchomeronic acid is presumably related to that of nicotinic or *iso*nicotinic acid, being either dimeric, or polymeric with the formation of unending two-dimensional sheets or layers. (cf. Banerjee and Rây, *loc. cit.*). All the argentic complexes, as expected, are paramagnetic with a moment value of approximately 1.73 μ_B.

Dübsky and Okác (*Coll. Czech. Chem. Com.*, 1931, **3**, 465), Lukes and Jurecek (*ibid.*, 1948, **13**, 131), as well as others have described Cu^{II} salts of many of these pyridine dicarboxylic acids. They have, however, found that in most cases the composition of the copper compound is given by one atom of copper combining with one of the acid molecule. But in the case of lutidinic (2 : 4), quinolinic (2 : 3) and dipicolinic (2 : 6) acids, copper compounds with two molecules of the acid per atom of copper have also been described. The compositions of these latter differ from their corresponding argentic compounds, as described here, in their water of hydration, which presumably accounts for their different X-ray pictures obtained for the compounds of quinolinic acid (2 : 3). Burada (*An. Sci. Univ. Jassey*, 1935, **20**, 71) described a silver^{II} quinolinate with one molecule of water, resembling the corresponding copper compound. We have, however, failed to verify this, as the silver complex prepared by us has always been found to contain two molecules of water of hydration.

Experimental

All the complex argentic compounds of pyridine dicarboxylic acids were prepared by adding the finely powdered acid to the solution of sodium or potassium persulphate almost simultaneously with silver nitrate solution, while the mixture was constantly stirred by means of a magnetic stirrer. The stirring was continued for about 3 hours for complete oxidation. It should, however, be noted that silver nitrate and the acid should not be allowed to come together in the absence of persulphate, as in that case highly insoluble univalent silver salt of the pyridine carboxylic acid is formed, which it is very difficult to oxidise.

1. *Argentic Quinolinate.*—It was obtained by Burada (*loc. cit.*) by oxidising silver quinoline nitrate, $Ag(C_9H_7N)_2NO_3$, with an excess of ammonium persulphate in aqueous solution. The composition of his compound is given by $Ag^{II}(XH)_2.H_2O$.

In the present case, quinolinic acid was prepared by the oxidation of quinoline with alkaline potassium permanganate solution on the water-bath (Koenigs, *Ber.*, 1879, **12**, 983). For the preparation of the argentic quinolinate, quinolinic acid (0.6 g.) in a finely divided state was added to sodium persulphate (3 g.), dissolved in the minimum quantity of cold water, followed immediately by a solution of silver nitrate (0.3 g.) in a little water. The mixture was stirred continuously for 3 hours. The colour of the mixture gradually turned orange-red. When no further change had occurred, the product was filtered through sintered glass-bed filter, washed with cold water till free of sulphate, and then dried in a vacuum desiccator, placed in a refrigerator. Yield 0.7-0.8 g.

The orange-red crystalline product is very sparingly soluble in water. It is quite stable in dry air in the cold and remains unchanged even after 3 months. The substance is readily decomposed by acids and alkalies; it liberates iodine from acid solutions of potassium iodide. [Found: Ag(oxidimetric), 22.41; Ag(gravimetric), 22.83; C, 35.81. $Ag(C_7H_4NO_4)_2.2H_2O$ requires Ag, 22.69; C, 35.30%]. The substance was found to be paramagnetic. $\chi_m = 2.236 \times 10^{-6}$; χ_M (corr.) $= 1247 \times 10^{-6}$; $\mu_B = 1.743$.

2. *Argentic Cinchomeronate.*—Cinchomeronic acid was prepared by the oxidation of quinine in a boiling mixture of concentrated and fuming nitric acid for about 150 hours (Kass, *Monatsh.*, 1902, **23**, 252).

The argentic complex was prepared exactly in the same way as the argentic quinolinate described above, yield 0.8 g. The substance forms dark red crystals and is quite stable in the dry air for months. It behaves like the previous compound. It does not decompose even when heated to 70° for one hour and is unaffected by light. [Found: Ag(oxidimetric), 24.41; Ag(gravimetric), 24.70; C, 38.98. $Ag(C_7H_4NO_4)_2$ requires Ag, 24.54; C, 38.18%]. $\chi_m = 2.434 \times 10^{-6}$; χ_M (corr.) $= 1232 \times 10^{-6}$; $\mu_B = 1.742$.

3. *Argentic* iso*Cinchomeronate.*—*iso*Cinchomeronic and lutidinic acids were prepared by the oxidation of a mixture of 2:5- and 2:4-dimethylpyridine (commercially available) with potassium permanganate solution on a water-bath with mechanical stirring (cf. Garkow, *Ber.*, 1904, **37**, 2063; Ladenburg, *Ber.*, 1885, **18**, 915). The dimethylpyridine mixture (10 g.) was oxidised with $KMnO_4$ (72 g.) in aqueous solution. After complete oxidation, when the colour of the permanganate disappeared, the mixture was filtered from the precipitated oxides of manganese. The clear colorless filtrate was cooled to 10° and acidified with HCl (indicated by Congo-red), when a heavy white precipitate of the mixture of 2:4- and 2:5-pyridine dicarboxylic acids separated out. These were then separated from each other by repeated extraction with hot water. The 2:4-acid (lutidinic acid), soluble in hot water, was freed from the admixture of 2:5-acid (*iso*cinchomeronic acid), the latter is difficultly soluble even in boiling water. The purity of the products was verified by determination of their melting points.

For the preparation of argentic complex of *iso*cinchomeronic acid, 0.413 g. of the acid was employed for 0.3 g. of $AgNO_3$ and 3 g. of sodium persulphate; yield 0.6 g. The preparation was carried out at 30° and the stirring was continued for about 5 hours. As the acid is highly insoluble, any excess should be carefully avoided.

The substance forms brick-red powder, insoluble in water; it is quite stable in air and remains unchanged for months. Its properties are similar to those of the previous compounds. [Found: Ag (oxidimetric), 24.21; Ag (gravimetric), 24.36; C 38.12. $Ag(C_7H_4NO_4)_2$ requires Ag, 24.54; C, 38.18%]. $\chi_m = 2.346 \times 10^{-6}$; χ_M (corr.) $= 1194 \times 10^{-6}$; $\mu_B = 1.712$.

4. *Argentic Lutidinate.*—The complex argentic compound of lutidinic acid (2:4) was prepared like the previous compound, using the same quantity of materials. The colour and other properties are closely allied to those of argentic *iso*cinchomeronate.

[Found: Ag (oxidimetric), 24.18; Ag (gravimetric), 24.66; C, 38.08. $Ag(C_7H_4NO_4)_2$ requires Ag, 24.54; C, 38.18%]. $\chi_m = 2.113 \times 10^{-6}$; χ_M (corr.) $= 1091 \times 10^{-6}$; $\mu_B = 1.644$.

5. *Argentic Dipicolinate.*—(*a*) *Green.* This was prepared like the previous compound, but the reaction temperature was maintained near about 15°. The mixture turned dark green with the separation of fine green crystals. Yield is almost the same as that of the argentic quinolinate.

The substance is moderately soluble in water, giving a green solution. In the solid state it is rather unstable except in the cold and dry state. When kept at the room temperature it gradually turns dark grey. [Found: Ag (oxidimetric), 21.15; Ag (gravimetric), 20.99; C, 33.02. $Ag(C_7H_4NO_4)_2.4H_2O$ requires Ag, 21.09; C, 32 81%]. $\chi_m = 2.2 \times 10^{-6}$; χ_M (corr.) $= 1252 \times 10^{-6}$; $\mu_B = 1.747$.

(*b*) *Chocolate.*—The preparation of this variety is similar to that of the green form, with this difference that the temperature is maintained at about 25°. From the green solution the product separated as a dark chocolate crystalline powder.

The substance, however, dissolves in water forming a green solution. It is somewhat more stable than the green form. In all other respects they behave alike. [Found: Ag (oxidimetric), 22.55; Ag (gravimetric), 22.83; C, 36.20; H, 2.65. $Ag(C_7H_4NO_4)_2.2H_2O$ requires Ag, 22.69; C, 35.30; H, 2 52%]. $\chi_m = 2.441 \times 10^{-6}$; χ_M (corr.) $= 1345 \times 10^{-6}$; $\mu_B = 1.807$.

The difference in colour of these two modifications is possibly caused by their difference in hydration, and the consequent difference in their crystal structure as revealed by their X-ray powder photographs (*vide infra*). There is no evidence, however, to prove that they might be related as *cis-trans* isomers of one and the same compound.

TABLE I

Argentic quinolinate, $2H_2O$ (Fig. 1).

θ.	d.	Intensity.	θ.	d.	Intensity.	θ.	d.	Intensity.
4°42	9.4004	80	14°8	3.1546	2	21°26	2.1064	5
6°18	7.0192	25	14°52	3.0021	5	21°43	2.0817	7
7°20	6.0354	40	15°11	2.9222	7	22°14	2.0356	25
8°5	5.4780	85	16°7	2.7749	25	23°3	1.9673	5
9°3	4.8968	1	16°52	2.6547	85	24°30	1.8574	20
9°49	4.5178	30	17°25	2.5735	2	25°54	1.7634	15
10°27	4 2458	10	18°12	2.4661	5	26°21	1.7354	2
11°30	3.8635	100	18°54	2.3779	7	26°59	1.6971	2
12°15	3.6302	25	19°56	2.2529	25	27°24	1.6737	1
12°21	3.6013	85	20°1	2.2502	5	27°52	1 6479	1
13°45	3.2407	1	20°30	2.1994	25	28°22	1.6213	

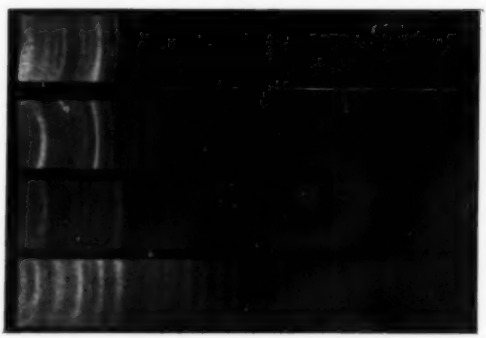

FIG. 1

FIG. 2

FIG. 3

FIG. 4

TABLE II

Copper quinolinate, H_2O (Fig. 2).

θ.	d.	Intensity.	θ.	d.	Intensity.	θ.	d.	Intensity.
5°52	7.5362	95	15°21	2.9098	25	21°49	2.0726	25
6°18	7.0192	95	16°21	2.7363	10	22°48	1.9877	7
6°31	6.7871	15	16°58	2.6396	5	23°12	1.9552	2
6°55	6.3963	20	17°24	2.5758	10	24°16	1.8742	2
11°21	3 9197	100	17°56	2.5016	10	24°45	1.8398	5
11°58	3 7154	15	18°25	2.4381	5	25°12	1.8091	5
12°52	3.4591	35	19°25	2.3170	15	25°58	1.7592	7
13°15	3.3507	5	19°58	2.2557	1	27°10	1.6871	20
14°1	3.1803	7	20°6	2.2412	10	28°3	1.6380	12
14°58	2.9825	2	21°10	2.1332	5	29°9	1.5813	18

TABLE III

Argentic dipicolinate, $4H_2O$ (*green*) (Fig. 3).

θ.	d.	Intensity.	θ.	d.	Intensity.	θ.	d.	Intensity.
4°21	10.1570	90	11°53	3.7406	2	20°36	2.1892	10
6°9	7.1903	95	12°17	3.6204	1	22°3	2.0518	1
7°12	6.1456	15	13°23	3.3277	100	22°39	2.0302	1
8°7	5.4556	1	14°29	3.0798	5	23°10	1.9578	10
9°5	4.8789	25	15°25	2.8975	1	24°37	1.8492	3
10°19	4.3011	25	16°28	2.7173	7	25°13	1.8080	1
11°18	3.9310	20	17°59	2.4948	10	26°10	1.7466	10
			19°25	2.3170	10			

TABLE IV

Argentic dipicolinate, $2H_2O$ (*chocolate*) (Fig. 4).

θ.	d.	Intensity.	θ.	d.	Intensity.	θ.	d.	Intensity.
4°18	10.273	85	11°48	3.7666	95	20°9	2.2359	40
5°36	7.8933	95	12°41	3 5081	1	21°35	2.0939	40
6°4	7.2886	1	13°36	3.2757	95	22°33	2.0086	5
7°33	5.8615	60	14°44	3.0287	2	23°19	1.9460	15
8°9	5.4335	60	15°27	2.8914	1	23°54	1.9012	5
9°1	4.9147	1	16°22	2.7335	1	24°51	1.8329	50
9°44	4.5561	100	17°8	2.6147	40	25°31	1.7881	3
10°42	4.1486	30	18°6	2.4793	40	26°9	1.7477	30
			18°48	2.3901	10			

X-ray measurements.—X-ray powder photographs of argentic quinolinate, $Ag(C_7H_4NO_4)_2.2H_2O$, and of the corresponding copper compound, $Cu(C_7H_4NO_4)_2.H_2O$, as well as of the green and chocolate modifications of argentic dipicolinate were taken in a cylindrical 9 cm Unicam camera with $Cu.K_\alpha$-radiation from Raymax demountable rotating anode tube at a voltage of 30 kV with a tube current of 50 mA. The time of exposure in each case was 3 hours.

It is evident from the measurement given above that cupric quinolinate and argentic quinolinate differ in their crystalline structure, as might be expected from the difference in their water of hydration. The two differently coloured modifications of argentic dipicolinate also show different structures, as already stated.

The authors desire to express their best thanks to Mr. B. Bishui of Glass and Ceramic Research Institute for the X-ray photographs, and to Dr. Atmaram, the Director of the Institute, for necessary permission.

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PHYSICO-CHEMICAL STUDIES ON AQUEOUS STEARIC ACID SOL. PART I

By R. S. Roy

The cataphoretic velocities of stearic acid sol particles at the room temperature ($25° \pm 2°$) with different concentrations of *n*-butylguanidine sulphate solution (*n*-BGS) have been determined by using a micro-electrophoretic cell. The change in the velocity at different time intervals has also been noted. The unusual velocity—concentration curve has been explained by assuming that the H^+ ions obtained from the acid dissociation form the outer part of the double layer and that envelops of water molecules or 'hydrospheres', which restrict the freedom of movement, exist round the colloidal particles.

Iyer *et al* (*Half-yearly J. Mysore Univ.*, 1932, **6**, 16, 188) observed that when $AlCl_3$ was rapidly added to a stearic acid sol in slight excess of that required for coagulation, a stable sol of opposite charge resulted, and they suggested the existence of transition layers between the phases, containing both adsorbed H_2O and oriented molecules of the non-aqueous solvent. From a study of the influence of H^+ and OH^- ions on colloidal stearic acid sol (*ibid.*, 1927, **1**, 183), Iyer *et al.* further pointed out that its behaviour illustrated the importance of hydration. Achar *et al.* (*J. Chem. Soc.*, 1927, 1875) have shown that when a stearic acid sol is treated with a neutral salt, acidity appears in the intermicellar liquid. Their observation suggests displacement by the salt cations of hydrogen ions produced by the ionisation of the surface molecules on the stearic acid particles.

From a recent study on the effect of cationic wetting agents on stearic acid sol, Roy *et al.* (*J. Indian Inst. Sci.*, 1955, **37A**, **B**, 4, 254) concluded that the added wetting agents formed a complex with the stearic acid molecules at the surface of the colloidal particles. The present paper deals with the cataphoretic study of stearic acid sol particles with *n*-BGS, with a view to elucidating the structure of the interface.

Experimental

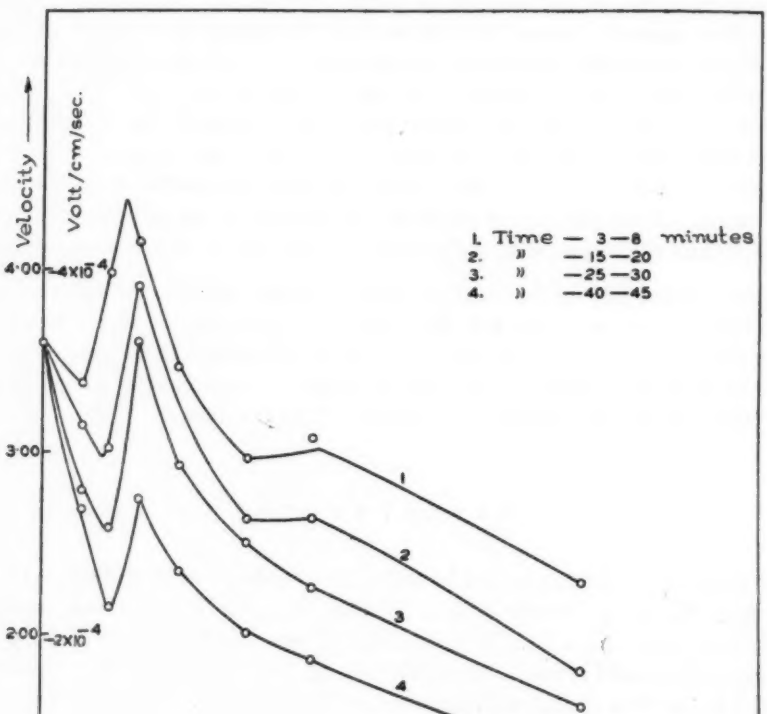
The stearic acid sol was prepared by following a method due to Mukherjee (*J. Mysore Univ.*, 1935, **1C**, 983). Stearic acid in alcohol (1 g. in 100 c.c.) was added dropwise to boiling water (400 c.c.). The resulting sol was freed from alcohol by further boiling and then filtered through Whatman No. 33 filter paper so as to avoid larger particles. It was then treated with 2 drops of 0.0005*N*-NaOH solution. The sol, thus prepared, was stable for many months and exhibited on shaking a streaky appearance.

n-Butylguanidine sulphate was prepared from *n*-butylamine and dimethyl*iso*thiourea sulphate by boiling with 50% aqueous alcohol and was recrystallised as needle-shaped crystals, m.p. 206°. The concentration of the aqueous solution of the sulphate was 4%.

A micro-electrophoretic cell with a cylindrical bore (Mattson's type) was employed in the present investigation. The instrument had the additional advantage of being provided with electrical connections by means of agar bridges. It was fixed to a wooden stand and illuminated by means of a point-o-lite lamp provided with a suitable condensing lens system. The voltage between the two agar bridges was measured using a calibrated voltmeter. Both the corrections due to Buswell and Larson (*J. Phys. Chem.* 1936, **40**, 833) and Henry (*J. Chem. Soc.*, 1938, 997) were incorporated with a view to obtaining the most accurate results with the micorophoretic cell.

The sol (10.0 c.c. of 0.00045%) was mixed with 5.0 c.c. of *n*-BGS in a bottle and the mixture was shaken almost uniformly for 1 minute. The sol was then transferred to the cataphoretic cell and the velocity of the particles was measured using direct as well as reverse current. An average value of six readings in each direction was taken. The velocities of the particles were recorded at definite time intervals and also with varying amounts of *n*-BGS.

FIG. 1



The results obtained are represented graphically in Fig. 1. The stearic acid sol in these experiments had a concentration of about 0.0003% while the *n*-BGS concentration varied from 0.1% to 1.3%. The curves exhibit some interesting features.

DISCUSSION

It is seen from Fig. 1 that the velocity of particles first decreases to a minimum at about 0.1 to 0.17% *n*-BGS and then rises up to a maximum at about 0.2 to 0.23%, followed by a gradual decrease.

Similar curves have also been observed with emulsions. While studying the cataphoretic velocity of saponin-stabilised emulsions of sodium oleate in the presence of electrolytes, King (*Trans. Faraday Soc.*, 1941, **37**, 174) observed a similar curve on the addition of $Al_2(SO_4)_3$. Size-frequency curves were also of the same type. He suggested that salting of the soap adsorbed at the surface was responsible for this effect. Powny and co-workers (*ibid.*, 1941, **37**, 152; 1937, **33**, 1243; 1940, **36**, 57) in their studies on the action of anionic wetting agents like sodium dodecyl sulphate on negatively charged emulsion (Nujol) obtained charges which were opposite to those mentioned above. They attributed the initial rise of the curve to the adsorption of the single long ions and subsequent fall to secondary adsorption of Na^+ ions. The further slow but definite rise was attributed to the formation of gegenions among the Na^+ ions.

As has been shown by Kruyt (Colloid Symposium Monograph, 1926, **4**, p. 304), the constancy of the dielectric constant of the medium cannot be assumed. In fact, KCl shows a minimum at 4-8 m*M*/litre.

The results can readily be explained in the light of the improved form of Smoluchowski's equation for large insulating particles. According to Henry (*Trans. Faraday Soc.*, 1948, **44**, 1024) and Booth (*ibid.*, p. 958) the velocity under unit potential gradient for large insulating particles is given by

$$\frac{U}{H} = \frac{D\xi}{4\pi\eta}\left[\frac{\mu_0 a}{\mu_0 a + \mu_s}\right]$$

where μ_0 = the specific conductivity of the fluid, μ_s = surface conductivity and a = radius of the particles. On the first addition of *n*-BGS, ξ diminishes appreciably, but the quantity in parenthesis remains almost unaltered (μ_0 remaining unchanged owing to the almost complete adsorption of the added *n*-BGS). Hence, first the value of U/H falls and the curve decreases. With further addition of it, ξ diminishes less rapidly while μ_0 increases, and 'a' may also increase due to partial coagulation. If the increase of $\mu_0 a/(\mu_0 a + \mu_s)$ outweighs the decrease of ξ, then the value of U/H increases and the curve will increase. With the addition of more and more of *n*-BGS solution, $\mu_0 a/(\mu_0 a + \mu_s)$ becomes almost constant (*i.e.*, unity), and hence, the value of U/H decreases in the same way as ξ decreases.

Another plaus.ble explanation can, however, be given as follows: Assuming that H^+ and Na^+ ions, obtained from the acid dissociation and from NaOH respectively, form the outer part of the double layer and that en elops of water molecules (hydrospheres), which restrict the freedom of movement, exist round the colloidal particles. On adding n-BGS at low concentrations, to start with, those simple guanidine ions, which possess a velocity greater than a critical value, their number being guided by the Maxwell's "Distribution law", dive deep into the double layer through the hydrosphere and form surface complex with the stearic acid molecules at the surface of the particles. Thereby, partial charge neutralisation takes place and the H^+ and Na^+ ions are partially expelled from the outer layer. Consequently, ξ and the thickness of the double layer decrease, resulting in a fall in the velocity. Afterwards the charged guanidine ions displace the water molecules and thus destroy the "hydrosphere". The particles now possess a greater velocity which might partly be due to the dehydration and partly due to the increase in the thickness of the double layer because of the presence of the guanidine ions in the outer layer. At higher concentrations, however, the guanidine ions get themselves adsorbed on the surface complex, and the thickness of the double layer decreases further (Bull and Gortner, *Proc. Roy. Soc.*, 1950, **201A**, 40).

In conclusion the author offers his grateful thanks to Prof. K. R. Krishnaswami aud Dr. M. R. A. Rao of the Indian Institute of Science, Bangalore, for their keen interest and kind encouragement and for presenting a micro-electrophoretic cell.

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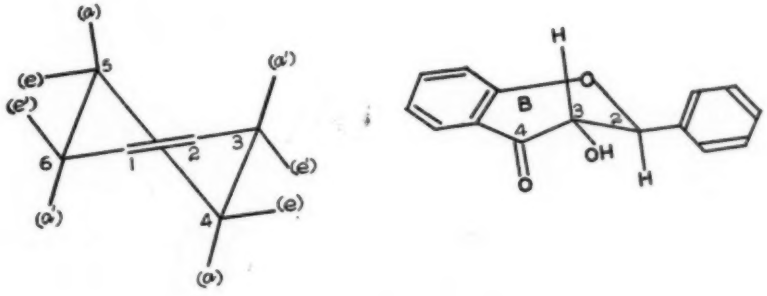
CO-ORDINATION BETWEEN DIFFERENT METHODS OF SYNTHESIS OF DIHYDROFLAVANOLS AND THEIR STEREOCHEMISTRY

By A. B. Kulkarni and C. G. Joshi

Stereochemical configurations assigned in a previous publication to dihydroflavanols are further supported by dehydrogenation data. The methods of synthesis of dihydroflavonols have been correlated by synthesising the same dihydroflavonol by two different methods.

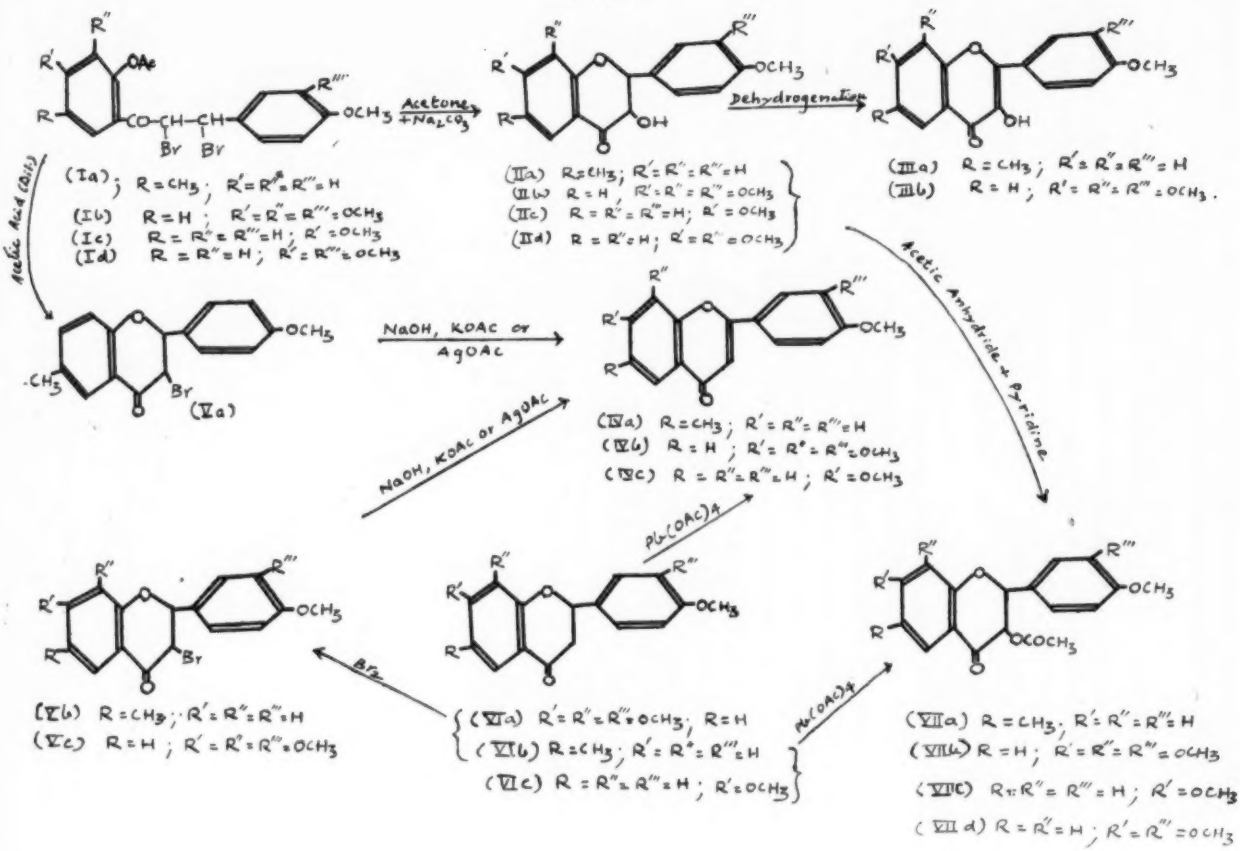
On the basis of the above findings, stereochemical configuration for both synthetic and natural dihydroflavonols is suggested. Incidentally, the conformations for C_3-OH and C_4-OH in melacacidin are tentatively assigned.

In previous communications (Kulkarni and Joshi, *Chem. & Ind.*, 1954, 1421, 1456) synthesis of dihydroflavonols and flavan-3 : 4-diols was reported and for the first time Barton's concept of conformational analysis (*J. Chem. Soc.*, 1953, 1027 ; *Chem. & Ind.*, 1954, 21) was introduced in this field to elucidate their stereochemistry. Dihydropyran ring of dihydroflavonols or flavan-diols was compared with *cyclo*hexene and it was pointed out that C_2 and C_3 positions in dihydropyran are identical with C_4 and C_5 carbon atoms in *cyclo*hexene. The bonds of the C_2 and C_3 carbon atoms were designated as equatorial and axial, and this terminology was adopted to understand the stereochemistry of substituents on these carbon atoms. It is obvious that the same concept can be utilised to understand the stereochemistry of catechins. In fact, this conformational aspect has been accepted and recently stereochemical configurations of catechin (Clark-Lewis, *Chem. & Ind.*, 1955, 1218), epicatechin (Roberts, *ibid.*, 1955, 631) and melacacidin (King and Clark-Lewis, *J. Chem. Soc.*, 1955, 3384) have been discussed in this direction.



Further, on the basis of the generalisation (Barton, *loc. cit.*) that, "a bulky substituent in a *cyclo*hexane ring system takes up an equatorial conformation as it is energetically most favourable arrangement", an equatorial conformation for the side phenyl nucleus in the dihydroflavonol was assigned (Kulkarni and Joshi, *loc. cit*). On reduction of 3′ : 4′ : 7 : 8-tetramethoxydihydroflavanol (IIb) with lithium aluminium hydride and catalytically, two compounds, m. p. 179° (XIIa) and 131-32° (XIIIa), isomeric in position "4", were isolated. The lower-melting compound, which was obtained in almost quantitative yield, when the dihydroflavonol was reduced catalytically in strongly acid

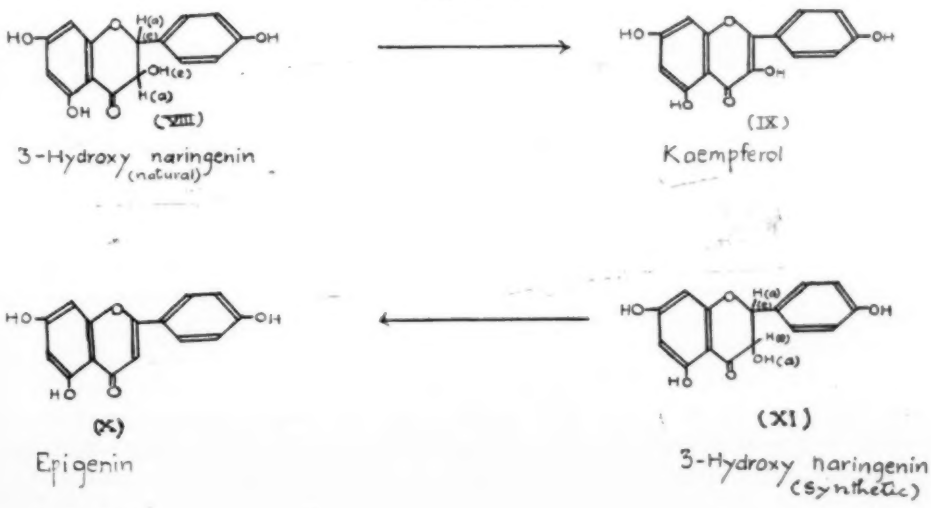
CHART I


Acetone + Na_2CO_3
Dehydrogenation
Acetic Acid (dil.)
NaOH, KOAc or AgOAc
Acetic Anhydride + Pyridine
$Pb(OAc)_4$
Br_2
(Ia); R = CH_3; R' = R'' = R''' = H
(Ib) R = H; R' = R'' = R''' = OCH_3
(Ic) R = R'' = R''' = H; R' = OCH_3
(Id) R = R'' = H; R' = R''' = OCH_3
(IIa) R = CH_3; R' = R'' = R''' = H
(IIb) R = H; R' = R'' = R''' = OCH_3
(IIc) R = R' = R''' = H; R'' = OCH_3
(IId) R = R'' = H; R' = R''' = OCH_3
(IIIa) R = CH_3; R' = R'' = R''' = H
(IIIb) R = H; R' = R'' = R''' = OCH_3.
(Ia)
(IVa) R = CH_3; R' = R'' = R''' = H
(IVb) R = H; R' = R'' = R''' = OCH_3
(IVc) R = R'' = R''' = H; R' = OCH_3
(Vb) R = CH_3; R' = R'' = R''' = H
(Vc) R = H; R' = R' = R''' = OCH_3
(Va) R' = R'' = R''' = OCH_3; R = H
(VIb) R = CH_3; R' = R'' = R''' = H
(VIc) R = R'' = R''' = H; R' = OCH_3
(VIIa) R = CH_3; R' = R'' = R''' = H
(VIIb) R = H; R' = R'' = R''' = OCH_3
(VIIc) R = R'' = R''' = H; R' = OCH_3
(VIId) R = R'' = H; R' = R''' = OCH_3

medium, was in accordance with the generalisation of Barton (*loc. cit.*) presumed to have C_4-OH axial. The other isomer therefore has C_4-OH equatorial. Further, on the assumption that the Auwers-Skita rule (*J. Chem. Soc.*, 1948, 1035) was applicable to these compounds, the higher-melting compound was assigned *trans* (2e, 3e, 4e) configuration and the lower-melting one as *cis* (2e, 3e, 4a) configuration (data such as velocity of hydrolysis of diacetates, behaviour of isomers on chromatographic column, formation of cyclic carbonate from the "cis" *i.e.* lower-melting isomer etc. supporting the above configurations will be published elsewhere). Thus, indirectly the conformation for C_3-OH group in the dihydroflavonol as equatorial was arrived at. This conformation for C_3-OH in dihydroflavonol was further supported by the fact that none of our diols were identical with (±) malacacidin tetramethyl ether (XIVa), synthesised by King and Clark-Lewis (*loc. cit.*) and assigned 2e, 3e, 4e conformation, which was also independently arrived at by us.

These investigations were further extended with a view to synthesing epimeric dihydroflavonol with C_3(OH) axial and thence the corresponding remaining two racemates of flavan-3 : 4-diols. It was thought that two 3-bromoflavanones, isomeric in position '3', recently reported by Limaye and co-workers (*Rasayanam*, 1950-52, **2**, 1, 51), would serve as intermediates for this purpose. Accordingly, 6-methyl-4′-methoxy-3-bromoflavanone (Vb, m.p. 152°), obtained by bromination of the corresponding flavanone, and its isomer (Va, m.p. 138°), obtained by cyclisation of the corresponding 2′-acetoxychalkone dibromide (Ia), were synthesised. The stereochemical configurations of these 3-bromoflavanones will be reported elsewhere. Both these compounds on treatment with common reagents used for the replacement of bromine with hydroxy or acetoxy group should give different dihydroflavonols, but unfortunately they are easily dehydrobrominated to the same corresponding flavone. Similarly, the 3-bromoflavanone (Vc), obtained on bromination of 3′ : 4′ : 7 : 8-tetramethoxyflavanone (VIa) with *N*-bromosuccinimide, is dehydrobrominated to the corresponding flavone (IVb). Since this method

CHART II



was unsuitable for the synthesis of epimeric dihydroflavonol and thence the other two racemic flavandiols, all the methods for the synthesis of dihydroflavonols were reviewed. The identical dihydroflavonols were synthesised by two different methods and thus the methods were correlated. We have been so far unable to synthesise epimeric (±) 6-methyl-4′-methoxydihydroflavonol by any ot these methods. However, the established co-ordination amongst the methods of synthesis and the dehydrogenation data on dihydroflavonols enable us to assign conformations to both synthetic and natural dihydroflavonols ; this communication deals with this aspect of the chemistry of dihydroflavonols.

The following methods are generally used for the synthesis of dihydroflavonols :—

(1) Flavanone $\xrightarrow{Pb(OAc)_4}$ dihydroflavonol (Oyamada, *J. Chem. Soc., Japan*, 1943, **64**, 331, 471).

(2) Chalkone $\xrightarrow{H_2O_2+alkali}$ dihydroflavonol (Murakami and Irie, *Proc. Imp. Acad. Tokyo*, 1935, **11**, 229 ; Riechel and Steudel, *Annalen*, 1942, **553**, 83).

(3) Chalkone acetate $\xrightarrow{Br}$ dibromide $\xrightarrow{\text{acetone-sodium carbonate}}$ dihydroflavonol (Limaye, *Rasayanam*, 1950, **2**, 1).

(4) Diacetoxychalkone $\xrightarrow{HCl}$ dihydroflavonol (Oyamada, *J. Chem.Soc. Japan*, 1934, **55**, 785)*.

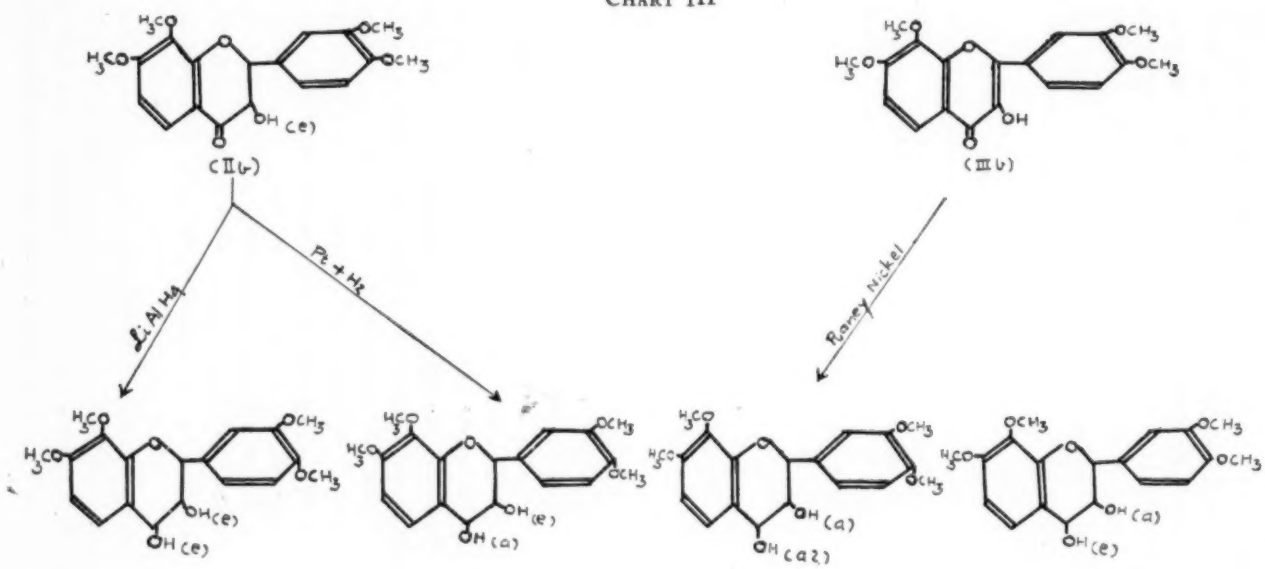
(5) Flavanol $\xrightarrow{\text{sodium hydrosulphite}}$ dihydroflavonol (Pew, *J. Amer. Chem. Soc.*, 1948, **70**, 3031).

(6) Flavanone $\xrightarrow{halogen}$ 3-halogenoflavanone $\xrightarrow{AgOAc}$ dihydroflavonol (Zemplen and Bognar, *Ber.*, 1943, **76B**, 452 ; Seshadri *et. al.*, *Proc. Ind. Acad. Sci.*, 1954, **39A**, 254).

(7) Flavonol $\xrightarrow{hydrogenation}$ dihydroflavonol, flavandiol (King *et al.*, *Chem & Ind.*, 1954, 757 ; *J. Chem. Soc.*, 1954, 1399).

The same dihydroflavonol acetates, *i.e.*, 6-methyl-4′-methoxy-(VIIa) and 7 : 4′-dimethoxy-(VIIc), were synthesised by us by methods (1) and (3). Similarly (±) fustin trimethyl ether (VIId), synthesised by Oyamada (*Annalen*, 1939, **533**, 441) by the method (4) and proved to be identical with the natural product, has also been obtained in this Laboratory by the method (3). Limaye and co-workers (*Rasayanam*, 1952, **2**, 51) reported the synthesis of the dihydroflavonol, *i.e.* 4′-methoxy-6-benzoyldihydroflavanol by methods (2) and (3). Synthetic (±) taxifolin, which, on the basis of dehydrogenation data, we think belongs to the first series, was obtained by the reduction of quercetin with sodium hydrosulphite (Pew, *loc. cit.*), *i.e.* by the method (5), and was shown to be identical with the natural one by Pew. We therefore believe that the dihydroflavonols synthesised by methods 1, 2, 3, 4 and 5 belong to the same series, *i.e.*, C_2-phenyl and C_3-OH in them are equatorial. Such a configuration would be energetically most stable and therefore it is no wonder that all the above methods give dihydroflavonols which belong to the same series. Seshadri *et al.* (*loc. cit.*) observed that synthetic 3-hydroxynaringenin (XI), obtained through 3-iodoflavanone, *i.e.*, by method (6), was different from

CHART III



(XII a) Diol, m.p. 179° ; (XIII a) Diol, m.p. 132° ; (±) (XIV a) King's diol, m.p. 135-6° ; (−) (XV a) Melacacidin tetramethylether. m.p. 145°-6

(XII b) Diacetate m.p. 120-21° ; (XIII b) Diacetate; m.p. 122° ; (±) (XIV b) " diacetate, m.p. 156°7; (−) (XV b) Melacacidin tetramethyl--ether diacetate, m.p. 193-4°.

the natural one (VIII) which, we believe, belongs to the first series (*vide infra*). Flavan-diols (Kulkarni and Joshi, *loc. cit.*) (XIIa) and (XIIIa), isomeric in position-4, synthesised by us from the corresponding dihydroflavonol, which is prepared by the method (3), are different from that (XIVa), synthesised by King *et al.* by hydrogenation of the corresponding flavonol (*private communication* from Dr. Clark-Lewis, for which we are grateful to him). It is therefore obvious that the flavan-diol of King is isomeric in position-3, *i.e.*, C_3-OH is axial and hence in the corresponding dihydroflavonol would also be axial. We therefore believe that the dihydroflavonols synthesised by methods (6) and (7) would belong to the second series (*i.e.* C_3-OH in them would be axial). Incidentally, this inference and the chemical evidence of King *et al.* (*loc. cit.*) that melacacidin forms a cyclic carbonate, enable us to suggest conformations for C_3-OH and C_4-OH in melacacidin as axial and equatorial respectively.

The above generalisations are supported by the dehydrogenation experiments carried out by us on some of the dihydroflavanols, synthesised in this laboratory and by Seshadri *et al.* (*loc. cit.*) on natural and synthetic 3-hydroxynaringenin. On boiling with alcoholic sulphuric acid, 6-methyl-4′-methoxydihydroflavanol (IIa m.p. 160°) (Kulkarni and Joshi, *loc. cit.*), 3′:4′:7:8-tetramethoxydihydroflavanol (IIb, m.p. 166°) (Kulkarni and Joshi, *loc. cit.*) and 3-hydroxynaringenin (VIII) (Seshadri *et al.*, *loc. cit.*) are dehydrogenated to 6-methyl-4′-methoxyflavonol (IIIa, m.p. 192°) (Limaye, *loc. cit.*, p. 1), 3′:4′:7:8-tetramethoxyflavonol (IIIb, m.p. 221°) (Kostanecki and Rudse, *Ber.*, 1905, **38**, 935) and Kaempherol (IX) (Seshadri *et al.*, *loc. cit.*) respectively, while the epimeric dihydroflavonol-synthetic 3-hydroxynaringenin (XI) gets dehydrated to furnish epigenin (X) (Seshadri *et al.*, *loc. cit.*). Mechanism suggested for dehydrogenation of dihydroflavonols by Asahina (*J. Pharm. Soc. Japan*, 1928, **48**, 1081) *i.e.*, C_2-H is oxidised to C_2-OH [in our opinion C_2-H(a) $\longrightarrow$ C-OH(a) by radical mechanism] and dehydration between C_2-OH and C_3-(H), *i.e.*, dehydrogenation of the original dihydroflavonol takes place, can be explained on *trans* (a, a)-elimination principle. Barton (*loc. cit.*) has reported that for ready 1:2-elimination reactions of ionic type, both the substituents in the *cyclo*hexane system should be *trans* and axial. According to our hypothesis C_2-H(a) oxidised to C_2 OH(a) and C_3-H in the first series are *trans* and axial, and hence, dehydration product or dehydrogenation of dihydroflavanol should be favoured, as observed above. Recent observations of Robertson *et al.* (*J. Chem. Soc.*, 1954, 4573) that 3-hydroxyflavanone prepared by the method (1) could not be dehydrated to the flavone further supports our hypothesis. In the second series C_2-H and C_3-OH are *trans* and axial, and hence, dehydration should be facilitated, as has been experimentally observed in the case of synthetic 3-hydroxynaringenin (Seshadri *et al.*, *loc. cit.*). Alkaline reagents (Gripenberg and Silander, *Chem. & Ind.*, 1955, 443 and the references cited therein) are rather drastic and likely to bring about isomerisation or epimerisation, and hence, dehydrogenation in their presence is not taken into consideration.

On the basis of the methods of synthesis and dehydrogenation data, the synthetic and natural dihydroflavanols, tabulated below, are provisionally assigned the following conformations. From Table I it can be inferred that naturally occurring dihydro-flavonols belong to the first series. Wide occurrence in nature of these dihydroflavonols

i.e., with C_2-phenyl and C_3-OH, both equatorial, would be expected, as such an arrangement would be the most thermodynamically stable. In view of the relationship, recently established between alpinone (Kotake, Sakan and Kubota, *Chem. & Ind.*, 1954, 1562) and pinobanksin (Lindstedt, *Acta Chem. Scand.*, 1950, **4**, 772), we believe that the latter belongs to the same series as alpinone, which is synthesised by method (2), and hence, included in the first series. The dehydrogenation data (Lindstedt, *loc. cit.*) on pinobanksin, which suggests its inclusion in the second series, therefore probably requires recheck-up.

TABLE I

Dihydroflavanol.	Nature.	Method of synthesis.	Dehydrogenation or dehydration with H_2SO_4.	Conformation for C_3-OH.
1st Series :				
1. 6-Methyl-4′-methoxy[1]	Synthetic	2 & 3	Dehydrogenation	e
2. 7 : 4′-Dimethoxy[1]	,,	2 & 3	Not known	e
3 3′ : 4′ : 7 : 8-Tetramethoxy[1]	,,	3	Dehydrogenation	e
4. 6 Benzoyl-4′-methoxy[4]	,,	1 & 3	Not known	e
5. Fustin trimethyl ether[5]	,,	3 & 4	Do	e
6. Taxifolin[6]	Natural	...	Dehydrogenation	e
	Synthetic	5		
7. Dihydrorobinetin[7]	Natural	...	Do	e
8. 3-Hydroxynaringenin[9]	,,	...	Do	e
9. Alpinone[3]	,,	...	Not known	e
	Synthetic	2		
10. Pinobanksin[8]	Natural converted to alpinone[3]		No dehydrogenation (?)	e
2nd Series :				
11. 3-Hydroxynaringenin[9]	Synthetic	6	Dehydration	a
12. 3-Hydroxyhesperitin[9]	Synthetic	6	Not known	a

1. Kulkarni & Joshi, *loc. cit.*
2. Oyamada, *loc. cit.*, 1934
3. Kotake, *et al.*, *loc. cit.*
4. Limaye, *loc. cit.*, p. 51.
5. Oyamada, *loc. cit.*, 1939
6. Pew, *loc cit.*
7. Freudenberg & Hartmann, *Annalen* 1954, **587**, 207.
8. Lindstedt, *loc. cit.*
9. Seshadri *et al.*, *loc. cit.*

Attempts are being made to collect more data by synthesising a number of dihydroflavonols, particularly by methods (6) and (7). Ozonolysis experiments on dihydroflavonols are in progress with a view to assigning them both the relative and absolute configurations.

EXPERIMENTAL

6-Methyl-4′-methoxydihydroflavanol (IIa).—2′-Hydroxy-5′-methyl-4-methoxychalkone (m.p. 97-99°), prepared by the condensation of 2-acetyl-*p*-cresol and anisaldehyde, was acetylated and then brominated to dibromochalkone (Ia) (Auwers and Anschutz, *Ber.*, 1921, **54**, 1543), m.p. 126°. It (1 g.) was then converted into the corresponding dihydroflavanol by boiling with aqueous acetone (10 c.c., 60%) for 10 minutes (Limaye, *loc. cit.*, p. 1) and then with sodium carbonate (10 c.c., 10%). On cooling, the oil separated and solidified. It was filtered and crystallised twice from alcohol, m.p. 160°, yield 0.4 g.

6-Methyl-4′-methoxy-3-acetoxyflavanone (VIIa): *Method* (1).—The dihydroflavanol (IIa: 200 mg.), dissolved in acetic anhydride (2 c.c.) and pyridine (1 c.c.), was kept overnight and then poured in water. The resulting solid was filtered and crystallised twice from alcohol, m.p. 133°, yield 0.15 g. (Limaye, *loc. cit.*, records m.p. 140°). (Found: C, 69.98; H, 5.63. Calc. for $C_{19}H_{18}O_5$: C, 69.94; H, 5.52%).

Method (2).—To a solution of 6-methyl-4′-methoxyflavanone (m.p. 110°) 1 g.) in glacial acetic acid (50 c.c.) was added lead tetra-acetate (2.4 g., 1.5*M*) in small portions during 45 minutes. During this period the temperature was maintained at 80-90° and the mixture was further heated at the same temperature for 4 hours. It was poured in water, extracted with ether and the ethereal extract was washed with water, dried over anhydrous sodium sulphate and the ether evaporated. The residue was crystallised twice from alcohol, m.p. 133°, yield 60 mg. (Found: C, 70.08; H, 5.54. Calc. for $C_{19}H_{18}O_5$: C, 69.94; H, 5.52%). Mixed m.p. with the one obtained by method (1) showed no depression.

The mother-liquors of crystallisation were combined and evaporated. The residue was crystallised from petroleum ether (b.p. 40°-60°) when a compound melting at 170° was obtained in poor yield. This was identified as 6-methyl-4′-methoxyflavone (IVa).

Dehydrogenation of (IIa).—The dihydroflavanol (IIa, 0.35 g.) was dissolved in alcohol (140 c.c.) and 4*N*-H_2SO_4 (35 c.c.) was added to it and refluxed in a current of oxygen for 24 hours, and the solvent evaporated. The residue was washed with water and crystallised from alcohol, m.p. 192°, yield 0.22 g. It was identified as 6-methyl-4′-methoxyflavonol (IIIa).

3-Bromo-6-methyl-4′-methoxyflavanone (Va)*.—2′-Acetoxy-5′-methyl-4-methoxychalkone dibromide (0.47 g.) was dissolved in warm dilute acetic acid (2 c.c., 85%) and kept overnight, when crystals separated. These were filtered, washed and crystallised from alcohol, m.p. 138°, yield 0.25 g.

3-Bromo-6-methyl-4′-methoxyflavanone (Vb)**.—6-Methyl-4′-methoxyflavanone (1.08 g.) was dissolved in acetic acid (2 c.c.) and to its boiling solution was added bromine in acetic acid (2.6 c.c., 25%). After two hours crystals separated, which were filtered, washed and recrystallised from alcohol, m.p, 152°, yield 1 g. (Found: C, 58.78; H, 4.59. Calc. for $C_{17}H_{15}O_3Br$: C, 58.8; H, 4.3%).

Action of NaOH *solution on 3-Bromoflavanones.*—(*a*). The alcoholic solutions of the 3-bromoflavanones (m.p. 138° and 152°) were treated with 10*N*-NaOH when a yellow precipitate separated in few minutes. It was filtered, washed with water, crystallised from alcohol and identified as the corresponding flavone, m.p. 170°.

(*b*). *Action of Potassium Acetate on the 3-Bromoflavanones.*—The alcoholic solutions of the above 3-bromoflavanones were refluxed with potassium acetate for 4 hours and poured in water. The precipitate was filtered, washed with water and crystallised from alcohol, and identified as the corresponding flavone, m.p. 170°.

* This was prepared by the method described in the Ph. D. thesis submitted to the University of Poona by G. V. Bhide.

** Melting point 152° could not be raised to 168°, as reported in the thesis.

(*c*). *Action of Silver Acetate on the 3-Bromoflavanones.*—The alcoholic solutions of the 3-bromoflavanones were refluxed with silver acetate for 4 hours and filtered. The solution was diluted and the precipitate was crystallised from alcohol. From the crystals, separated in the first crop, the bromo compounds were recovered unchanged. The mother-liquors were evaporated and the residue recrystallised from alcohol, when a little amount of the corresponding flavone, m.p. 170°, was obtained.

In the experiments carried out in acetic acid, the major product was 6-methyl-4′-methoxyflavone, m.p. 170°.

2′-*Acetoxy*-3′:4′-3:4-*Tetramethoxychalkone* (Ib).—The chalkone (m.p. 125-27°) (5 g.) was heated with fused sodium acetate (50 mg.) and acetic anhydride (8 c.c.) for one hour. The reaction mixture was poured in water and the resulting solid was filtered and crystallised from alcohol, m.p. 125°. It gave no coloration with alcoholic ferric chloride and was insoluble in dilute aqueous alkali. (Found: C, 65.48; H, 6.17; Calc. for $C_{21}H_{22}O_7$: C, 65.29; H, 5.69%).

3′:4′-7:8-*Tetramethoxydihydroflavanol* (IIb).—The above chalkone (0.6 g.) was dissolved in CCl_4 (12.5 c.c.) and a solution of bromine in CCl_4 (1 c.c., 25%) was added. After two hours the solvent was evaporated under reduced pressure. The residue was boiled with aqueous acetone (80%, 10 c c.) for 13-16 minutes and subsequently with sodium carbonate (10%, 10 c.c.) for 3 minutes. On cooling, the oil separated and solidified. It was filtered and crystallised twice from alcohol, m.p. 166°, yield 0.2 g. (Found: C, 63.55; H, 5.66. Calc. for $C_{19}H_{20}O_7$: C, 63.33: H, 5.55%).

It gave no coloration with alcoholic ferric chloride. It, however, gave an orange coloration with H_2SO_4 (conc.) and a pink coloration with alcoholic zinc-hydrochloric acid.

3′:4′-7:8-*Tetramethoxy*-3-*acetoxyflavanone* (VIIb).—The dihydroflavanol (IIb: 200 mg.) was dissolved in acetic anhydride (4 c.c.) and pyridine (2 c.c.) and kept overnight. The solution was poured in water and extracted with ether. The ether extract was washed with water, dried over anhydrous sodium sulphate, and the ether distilled over. The residue was crystallised thrice from 70% alcohol, m.p. 113-16° (100 mg.). (Found: C, 62.23; H, 5.94. Calc. for $C_{21}H_{22}O_8$: C, 62.69; H, 5.47%).

Dehydrogenation of (IIb).—The dihydroflavanol (IIb: 100 mg.) was dissolved in alcohol (15 c.c.) and 4*N*-H_2SO_4 (15 c.c.) was added to it. The solution was refluxed for 4 hours in a current of oxygen. It was cooled and the precipitate was filtered, washed with water and crystallised from alcohol, m.p. 221°, yield 40 mg. Mixed m.p. with 3′:4′-7:8-tetramethoxyflavonol (IIIb) (Kostanecki and Rudse, *loc. cit.*) gave no depression.

Bromination of 3′:4′-7:8-*Tetramethoxyflavanone and the Action of Silver Acetate on the Bromo Compound.*—3′:4′-7:8-Tetramethoxyflavanone (m.p. 144°) (0.8 g.) was dissolved in a mixture of CCl_4 and $CHCl_3$ (1:1; 40 c.c.) and *N*-bromosuccinimide (1*M*) was added to it. The mixture was refluxed for 30 minutes in presence of light and the resulting precipitate was filtered, washed with CCl_4 and dried, m.p. 175°, yield 0.2 g.

The bromo compound (Vc, 0.2 g.) was dissolved in acetic anhydride (10 c.c.) and silver acetate (0.2 g.) was added to it. The mixture was refluxed for 2 hours on a water-bath and 1 hour in an oil-bath (145-55°). It was filtered and the filtrate diluted with

cold water, when a precipitate was obtained. It was crystallised from alcohol, m.p. 199-200°, yield 50 mg. Venkataraman *et al.* (*J. Chem. Soc.*, 1932, 1107) reported for 3′:4′-7:8-tetramethoxyflavone (IVb), m.p. 199°.

The substance was free from bromine and gave a red coloration with alcoholic zinc-hydrochloric acid, and hence, a flavone. (Found: C, 66.77; H. 5 4. Calc. for $C_{19}H_{18}O_6$: C, 66.82; H, 5.26%).

7:4′-*Dimethoxydihydroflavanol* (IIc).—2′-Hydroxy-4:4′-dimethoxychalkone (m.p. 113-14°) (50 g.), prepared by the method of Kostanecki *et al.* (*Ber.*, 1899, **32**, 322), was acetylated by boiling for 2 hours with acetic anhydride (2 c.c.) and fused sodium acetate (few mg.). The solution was cooled and acetic acid (0.5 c.c.) and bromine in acetic acid (1.12 c.c., 25%) were added to it. After two hours, the solution was diluted with water, when a white precipitate was obtained (900 mg.). It was boiled with aqueous acetone (10 c.c., 80%) for 15 minutes and subsequently with sodium carbonate (10 c.c., 10%) for 3 minutes. On cooling, the oil separated and solidified. It was filtered and crystallised thrice from alcohol (Ic), m.p. 133°, yield 200 mg. It gave no coloration with alcoholic ferric chloride, but a violet colour with zinc-hydrochloric acid. (Found: C, 67.88; H, 5.27. Calc. for $C_{17}H_{16}O_5$: C, 68.0; H, 5.33%).

7:4-*Dimethoxy*-3-*acetoxyflavanone* (VIIc): *Method* (1).—7:4′-Dimethoxydihydroflavanol (0.2 g.) was dissolved in acetic anhydride (40 c.c.) and pyridine (1 c.c.) and kept overnight. The solution was poured in water and extracted with ether. The ether extract was washed with water, dried over anhydrous sodium sulphate and evaporated. The residue was crystallised thrice from alcohol, m.p. 140-42°. (Found: C, 66.24; H, 5.19. Calc. for $C_{19}H_{18}O_6$: C, 66.66; H, 5.26%).

Method (2).—To a solution of 7:4′-dimethoxyflavanone (VIc, 0.8 g.) (Kostanecki and Juppen, *Ber.*, 1904, **37**, 4161) in acetic acid (50 c.c.) was added lead tetra-acetate (2 g.) in small portions and the same procedure was adopted as laid down under method (2) for (VIIa). The residue was crystallised twice from alcohol, m.p. 140-141°, yield 40 mg. Mixed m.p. with the one obtained by method (1) showed no depression. (Found: C, 66.41; H, 5.04. Calc. for $C_{19}H_{18}O_6$: C, 66.66; H, 5.26%).

The mother-liquors of crystallisation were combined and evaporated. The sticky residue was dissolved in minimum amount of benzene and the solution adsorbed over alumina. On elution with petroleum ether a substance melting at 144° was obtained in poor yield. It showed no depression in the mixed m p. with 7:4′-dimethoxyflavone (IVc) (Tambor, *Ber.*, 1916, **49**, 1704).

Fustin Trimethyl Ether (7:3′:4′-*Trimethoxydihydroflavanol*) (IId).—2′-Acetoxy-3:3:4′-trimethoxychalkone (Id, m.p. 87°), the starting material, was prepared by the method of Oyamada (*Annalen*, 1939, **538**, 441). This compound (0.6 g.) was dissolved in CCl_4 (10 c.c.) and bromine in CCl_4 (1.1 c.c., 25%) was added to it. After two hours the solvent was evaporated under reduced pressure. The residue was boiled with aqueous acetone (80%, 10 c.c.) for 13-15 minutes and subsequently with sodium carbonate solution (10 c.c., 10%) for 3 minutes. On cooling, the oil separated and solidified. It was filtered and crystallised thrice from alcohol, m.p. 143°, yield, 0.15 g. It gave a pink coloration with zinc-hydrochloric acid and no coloration with alcoholic ferric chloride. (Found: C, 65.22; H, 5.54. Calc. for $C_{18}H_{18}O_6$: C, 65.45; H, 5.45%).

7 : 3′ : 4′-Trimethoxy-3-acetoxydihydroflavanol (VIId).—The dihydroflavanol (IId : 0.2 g.) was dissolved in acetic anhydride (4 c.c.) and pyridine (1 c.c.) and kept overnight. The solution was poured in water and the product was extracted with ether. The ether extract was washed with water, dried over anhydrous sodium sulphate and evaporated. The residue was crystallised twice from alcohol, m.p. 145°, yield, 0.15 g. (Found : C, 64.72 ; H, 5.36. Calc. for $C_{20}H_{20}O_7$: C, 64.51 ; H, 5.36%).

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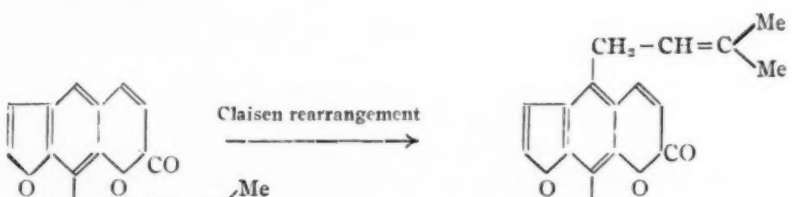
ISOLATION OF ALLO-IMPERATORIN AND β-SITOSTEROL FROM THE FRUITS OF *AEGLE MARMELOS* CORREA

By Sudhir Kumar Saha and (Mrs.) Asima Chatterjee

The fruits of *Aegle marmelos* Correa contain allo-imperatorin and β-sitosterol, besides imperatorin, a γγ-dimethylallyloxyfurocoumarin.

The fruit of *Aegle marmelos* Correa (N. O. *Rutaceae*), commonly known as *Bael*, possesses distinct medicinal values. It has been the subject of investigation by several workers (Dikshit and Dutt, this *Journal*, 1939, **7**, 579; 1932, **9**, 271) and the latest researches on it have revealed the presence of a furocoumarin, identified as imperatorin (I) (Späth, Bose, Guha and Grüber, *Ber.*, 1939, **70**, 1021).

The present authors have observed that the fruit pulp of *A. marmelos* contains allo-imperatorin [5-(γγ-dimethylallyl)-8-hydroxyfurocoumarin], (II), besides imperatorin (I) and β-sitosterol. A benzene solution of a concentrated alcoholic extract of the fruit pulp of *A. marmelos* yielded allo-imperatorin ($C_{16}H_{14}O_4$) in 0.003% yield. From its mother-liquor by chromatographic resolution (Chatterjee and Choudhury, *Naturwiss.*, 1955, **42**, 535) imperatorin ($C_{16}H_{14}O_4$) and β-sitosterol ($C_{29}H_{50}O$) were obtained in 0.006% and 0.00125% yield respectively.



(I) (II)

Allo-imperatorin dissolves in alcoholic caustic potash with a blue-violet fluorescence and a yellow solution which remains clear on dilution with water and reprecipitates the original compound unchanged on acidification with mineral acids. This furocoumarin produces a green coloration with alcoholic ferric chloride. With diazomethane it forms a monomethyl ether, $C_{16}H_{13}O_3.(OCH_3)$. Identity of this furocoumarin with allo-imperatorin has been established from their mixed m.p. determination and mixed chromatogram (an authentic sample of allo-imperatorin being prepared from imperatorin by Claisen rearrangement), and also by the negative depression in mixed m.p. of their monomethyl ether.

β-Sitosterol has been characterised from the studies of its elementary analyses, characteristic colour reactions with sterol reagents, mixed melting point determination and mixed chromatogram with an authenticsample of β-sitosterol.

EXPERIMENTAL

Isolation of Allo-imperatorin.—The fruit pulp of *A. marmelos* (4.0 kg.) was crushed in a Waring blendor in alcohol medium and kept for a month. It was then freed from alcohol under reduced pressure and soxhletted with benzene. The benzene layer after washing successively with 2*N*-HCl (4 × 50 c.c.) and water (2 × 50 c.c.), was dried over anhydrous sodium sulphate, concentrated to 50 c.c. and kept in a refrigerator for one week. A solid, m.p. 220-24° (decomp.), separated (A). Upon repeated crystallisation from 95% ethanol, the m.p. 226-27° (decomp.) of (A) did not change any more. It is fairly soluble in methanol, ethanol, benzene, but insoluble in ether and water. Mixed m.p. with an authentic sample of allo-imperatorin showed no depression. (Found : C, 71.35 ; H, 5.46. Calc. for $C_{16}H_{14}O_4$: C, 71.11 ; H, 5.18%).

Methylation of Allo-imperatorin.—Allo-imperatorin (0.05 g.), dissolved in dry methanol (5 c.c.), was treated with an excess of diazomethane at 0° and kept overnight. The solvent was removed and the residual solid crystallised from a mixture of benzene and petroleum ether (b. p. 40°-60°) in colorless crystals, m. p. 113°. (Found : -OMe, 10.98. $C_{16}H_{13}O_3$·OMe requires OMe, 10.90%).

Conversion of Imperatorin into Allo-imperatorin.—Imperatorin (0.1 g.) was taken in a distillation bulb and heated for 1 hour at 200-205°/3 mm. It was then sublimed at 200-10°/0.4 mm. The sublimate (0.095 g.) crystallised from 95% ethanol in plates, m. p. 226-27° (decomp.). Upon recrystallisation from the same solvent the m.p. did not change. (Found : C, 71.15 ; H, 5.58. Calc. for $C_{16}H_{14}O_4$: C, 71.11 ; H, 5.18%).

Isolation of Imperatorin and β-Sitosterol.—The mother-liquor left after the separation of allo-imperatorin (*vide supra*) was chromatographed over a column of Brockmann alumina (12 cm × 1 cm).

Elution with benzene (collected in fractions of 25 c.c. each) yielded from the first four fractions 0.25 g. of a material, which on three crystallisations from a mixture of petroleum ether (b.p. 40°-60°) and benzene (1 : 4) furnished colorless and fine needle-shaped crystals with a constant m.p. 101° (B). Mixed m.p. with an authentic sample of imperatorin did not show any depression. (Found : C, 71.05 ; H, 5.31. Calc. for $C_{16}H_{14}O_4$: C, 71.11 ; H, 5.18%).

On further elution with the same solvent, the fifth and the sixth fractions yielded 0.05 g. of a material which on repeated crystallisations from dry methanol furnished colorless flakes with constant m.p. 136-37° (C). The product, which was fairly soluble in benzene, methanol and ethanol and readily soluble in ether and ethyl acetate, did not depress the m.p. of an authentic sample of β-sitosterol. (Found : C, 84.02 ; H, 12.09. Calc. for $C_{29}H_{50}O$: C, 83.93 ; H, 12.15%).

Mixed Chromatogram of the Solid (A) and an authentic sample of Allo-imperatorin.—The solid A (0.02 g.), mixed with an equal quantity of an authentic sample

of allo-imperatorin, was taken in a minimum quantity of benzene and chromatographed over a column of alumina (9 cm. × 0.5 cm.). Elution with benzene yielded from the first two fractions 0.035 g. of a material which on crystallisation from ethanol furnished pure allo-imperatorin with a constant m.p. 226-27°.

Mixed Chromatogram of the Solid (C) and an authentic sample of β-Sitosterol.—The solid C (0.03 g.) with an equal quantity of an authentic sample of β-sitosterol was taken in minimum quantity of benzene and chromatographed over a column of Brockmann alumina (12 cm × 0.5 cm). Elution with benzene yielded from the first three fractions 0.05 g. of a material, which on repeated crystallisation from dry methanol furnished colorless flakes with constant m.p. 137°.

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THE CONDENSATION OF ALDEHYDES WITH β-KETO-ESTERS. PART III. 3-HYDROXY-, 4-HYDROXY- AND 3:4-DIHYDROXY-BENZALDEHYDES

By Miss Rajani K. Pandya and Kantilal C. Pandya

3 Hydroxy-, 4-hydroxy- and 3 : 4-dihydroxy-benzaldehydes have been condensed with ethyl acetoacetate and ethyl benzoylacetate in the presence of piperidine, pyridine and lutidine. The resulting *mono*- and *bis*-esters have been characterised.

In Parts I and II of this series (Pandya and Miss Pandya Jr., *Agra Univ. J. Res.*, 1955, **4**, 305, 345) salicyladehylde and nine of its derived aldehydes (including resorcylaldehyde) have been condensed with ethyl acetoacetate and ethyl benzoylacetate in the presence of piperidine, pyridine and 2:6-lutidine to obtain the corresponding coumarins. In the present paper this work has been extended to 3-hydroxy-, 4-hydroxy- and 3:4-dihydroxy-benzaldehydes. While condensations with ethyl acetoacetate have yielded two types of products, viz., (1) mono-esters (I) (substituted cinnamic esters) and (2) *bis*-esters (II), (substituted glutaric esters), depending on the quantity of the keto-ester used, only the mono-esters have been obtained in condensations with ethyl benzoylacetate.

The *bis*-esters from ethyl acetoacetate undergo ring-chain tautomerism (IIA) as well as keto-enol tautomerism (IIB). The cyclic tautomer itself affords other keto-enol tautomers in cyclic form. Though all these different open-chain and cyclic tautomers are not separable here, yet their presence is evident from the different open-chain and cyclic products obtained by hydrolysis. Also Knoevenagel (*Ber.*, 1896, **29**, 172) recorded one illustration of ethyl benzylidene-*bis*-acetoacetate, where out of the twelve possible tautomers (8 keto and 4 enol), six (3 keto and 3 enol) were separated by him and other workers.

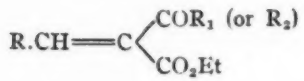
While the mono-esters from monohydroxybenzaldehydes had yielded the corresponding acids (III) on hydrolysis with 5-10% NaOH solution, those from dihydroxybenzaldehydes yielded only resins. The three β-(mono- or dihydroxyphenyl)-glutaric acids (IV) are obtained from the three *bis*-esters (II) even by mild alkali hydrolysis. Formation of these acids confirms the open-chain configuration of the *bis*-esters.

On treatment with phosphoric acid (cf. Horning and Field, *J. Amer. Chem. Soc.*, 1946, **68**, 384) the three *bis*-esters (II) gave the respective *cyclo*keto-di-esters (V), which were, however, not further hydrolysed to the cyclic ketones (cf. Knoevenagel, *loc. cit.*). Formation of these ketones confirms the cyclic configuration of the *bis*-esters.

The mono-esters (I) from both the keto-esters react with hydroxylamine to afford the corresponding *iso*xazolones (VI). The *bis*-esters (IIA, IIB) react with one mole of 2:4-dinitrophenylhydrazine to furnish the corresponding derivative.

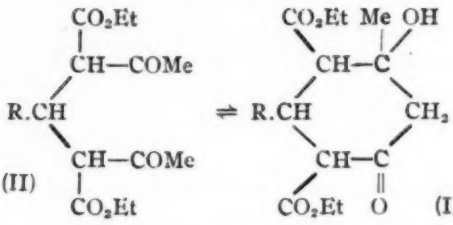
CHART I

Mono-esters:
Substituted cinnamic esters.

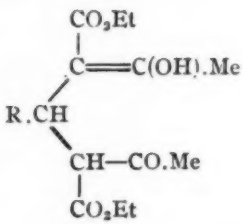


(I)

Bis-esters:
Substituted glutaric esters.

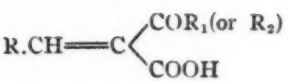


(II) (IIA)



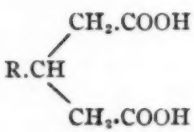
(IIB)

Substituted cinnamic acids.



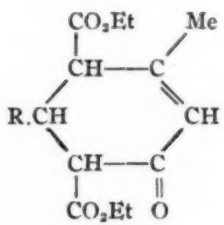
(III)

Substituted glutaric acids.



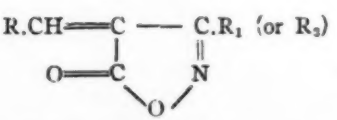
(IV)

*cyclo*Keto-di-esters.



(V)

*Iso*xazolones



(VI)

where R is, a = 3-OH.C_6H_4, b = 4-OH.C_6H_4, c = 3:4-$(OH)_2$.C_6H_3
R_1 = Me
R_2 = Ph

TABLE I

3-Hydroxybenzaldehyde : Condensations.

No.	Base.	Molar proportions.	Temp.	Time.	Ester.	Yield.	Temp.	Time.	Ester.	Yield.
			With ethyl acetoacetate.				With ethyl benzoylacetate.			
1.	Piperidine	1 : 1 : 0.1	20°	10 hrs.	Mono	86%	30°	20 hrs.	Mono	92%
2.	,,	1 : 2 : 0.1	20°	6	Bis	98	30°	24	,,	84
3.	Pyridine	1 : 1 : 6	Water-bath	24	Mono	56	Water-bath	16	,,	62
4.	,,	1 : 2 : 6	,,	24	,,	48	,,	16	,,	56
5.	Lutidine	1 : 1 : 3	,,	10	,,	68	,,	8	,,	74
6.	,,	1 : 2 : 3	,,	10	,,	52	,,	8	,,	64

TABLE II

Products from 3-hydroxybenzaldehyde.

	Products.	No.	M.P.	Cryst. shape.	Mol. formula.	Analysis (%). Found.	Calc.
1.	*Ethyl (3-hydroxybenzylidene)-*mono*-acetoacetate	I : R_1a	140°	White plates	$C_{13}H_{14}O_4$	C : 66.76 H : 6.00	66.66 5.98
2.	Ethyl (3-hydroxybenzylidene)-*mono*-benzoylacetate	I : R_2a	156°	White cubes	$C_{18}H_{16}O_4$	C : 72.90 H : 5.40	72 97 5.46
3.	Ethyl (3-hydroxybenzylidene)-*bis*-acetoacetate	II : a	170°	White tiny needles	$C_{19}H_{24}O_7$	C : 62.42 H : 6.58	62.63 6.59
4.	3-Hydroxybenzylidene-*mono*-acetoacetic acid	III : R_1a	118°	Yellow needles	$C_{11}H_{10}O_4$	C : 63.87 H : 4 9	64.07 4.8
5.	3-Hydroxybenzylidene-*mono*-benzoylacetic acid	III : R_2a	134°	White needles	$C_{16}H_{12}O_4$	C : 71.20 H : 4.25	71.6 4.5
6.	β-(3-Hydroxyphenyl)-glutaric acid	IVa	188° (eff)	White needles	$C_{11}H_{12}O_5$	C : 54.46 H : 5.3	54.4 5.3
7.	1-Methyl-3-(3-hydroxyphenyl)-2 : 4-dicarbethoxy-6-*cyclo*hexene-5-one	Va	80°	White prisms	$C_{19}H_{22}O_6$	C : 66.36 H : 6.86	66.04 6.36
8.	3-Methyl-4-(3-hydroxybenzylidenel)-*iso*xazolone-5	VI : R_1a	220° (decomp.)	Yellow cubes	$C_{11}H_9O_3N$	N : 7.0	6.9
9.	3-Phenyl-4-(3-hydroxybenzylidenel)-*iso*xazolone-5	VI : R_2a	197° (decomp.)	Pale yellow needles	$C_{16}H_{11}O_3N$	N : 5.4	5.28
10.	2 : 4-Dinitrophenylhydrazone.	From IIa	224° (decomp.)	Brick-red needles	$C_{23}H_{18}O_{10}N_4$	N : 10.16	10.29

*Also prepared by Gupta & Dutt (M.Sc. Theses, Agra Univ, 1946-47, unpublished).

TABLE III

4-Hydroxybenzaldehyde : Condensations.

No.	Base.	Molar proportions.	Temp.	Time.	Ester product.	Yield.
			With ethyl acetoacetate.			
1.	Piperidine	1 : 1 : 0.1	28°	3 hrs.	Mono	96 %
2.	,,	1 : 2 : 0.2	18°	72	Bis	86
3.	,,	1 : 1 : 0.1	18°	28	,,	98
4.	Pyridine	1 : 1 : 6	Water-bath	16	Mono	59
5.	,,	1 : 2 : 6	,,	16	,,	40
6.	,,	1 : 3 : 6	,,	16	Bis	40
7.	Lutidine	1 : 1 : 1	,,	6	Mono	26
8.	,,	1 : 1 : 3	,,	6	,,	86
9.	,,	1 : 2 : 3	,,	8	,,	51
			With ethyl benzoylacetate.			
1.	Piperidine	1 : 1 : 0.1	30°	10	Mono	98
2.	,,	1 : 2 : 0.1	30°	12	,,	95
3.	Pyridine	1 : 1 : 6	Water-bath	16	,,	66
4.	,,	1 : 2 : 6	,,	16	,,	48
5.	Lutidine	1 : 1 : 3	,,	8	,,	88
6.	,,	1 : 2 : 3	,,	8	,,	52

TABLE IV

Products from 4-hydroxybenzaldehyde.

	Products.	No.	M.P.	Cryst. shape.	Mol. formula.	Analysis (%). Found.	Calc.
1.	*Ethyl (4-hydroxybenzylidene)-*mono*-acetoacetate	I : R_1b	140°	Yellow plates	$C_{13}H_{14}O_4$	C : 67.03 H : 5.98	66.66 5.98
2.	Ethyl (4-hydroxybenzylidene)-*mono*-benzoylacetate	I : R_2b	180°	White cubes	$C_{18}H_{16}O_4$	C : 72.6 H : 5.2	72.07 5.46
3.	Ethyl (4-hydroxybenzylidene)-*bis*-acetoacetate	IIb	175°	White needles	$C_{19}H_{24}O_7$	C : 62.53 H : 6.54	62.63 6.59
4.	4-Hydroxybenzylidene-*mono*-acetoacetic acid	III : R_1b	121°	Yellow needles	$C_{11}H_{10}O_4$	C : 64.2 H : 4.8	64.07 4.8
5.	4-Hydroxybenzylidene-*mono*-benzoylacetic acid	III : R_2b	154°	White needles	$C_{16}H_{12}O_4$	C : 72.4 H : 4.6	71.6 4.5
6.	β-(4-Hydroxyphenyl)-glutaric acid	IVb	210° (eff.)	,, ,,	$C_{11}H_{12}O_5$	C : 54.26 H : 5.6	54.4 5.3
7.	1-Methyl-3-(4-hydroxyphenyl)-2 : 4-dicarbethoxy-6-*cyclo*hexene-5-one	Vb	98°	White prisms	$C_{19}H_{22}O_6$	C : 65.58 H : 6.3	66.04 6.36
8.	3-Methyl-4-(4-hydroxybenzylidenel)-*iso*xazolone-5	VI : R_1b	215° (decomp.)	Yellow cubes	$C_{11}H_9O_3N$	N : 6.68	6.9
9.	3-Phenyl-4-(4-hydroxybenzylidenel)-*iso*xazolone-5	VI : R_2b	206° (decomp.)	Pale yellow needles	$C_{16}H_{11}O_3N$	N : 5.16	5.28
10	2 : 4-Dinitrophenylhydrazone	From IIb	219° (decomp.)	Shining red needles	$C_{25}H_{28}O_{10}N_4$	N : 10.34	10.29

* Also prepared by Gupta & Dutt (*loc. cit.*).

TABLE V

3 : 4-Dihydroxybenzaldehyde : Condensations.

No.	Base.	Molar proportions.	Temp.	Time.	Ester product.	Yield.
			With ethyl acetoacetate.			
1.	Piperidine	1 : 1 : 0.1	18°	26 hrs.	Mono	80%
2.	,,	1 : 2 : 0.1	18°	20	Bis	83
3.	Pyridine	1 : 1 : 6	Water-bath	12	Resin	...
4.	,,	1 : 2 : 6	,,	12	,,	...
5.	,,	1 : 1 : 3	20-22°	3 weeks	Bis	24
6.	Lutidine	1 : 1 : 3 or 1 : 2 : 3	Water-bath or 60-70°	12-48 hrs.	Resin	...
7.	,,	1 : 1 : 3	20-22°	3 weeks	Bis	32.6
			With ethyl benzoylacetate.			
1.	Piperidine	1 : 1 : 0.1	28°	24 hrs.	Mono	72
2.	,,	1 : 2 : 0.1	28°	24	,,	89
3.	Pyridine	1 : 1 : 6	Water-bath	12-24	Resin	...
	,,	1 : 2 : 6	,,	12-24	...	...
4.	,,	1 : 1 : 3	26-28°	6 weeks	Mono	56
5.	Lutidine	1 : 1 : 3	Water-bath	5-24 hrs.	Resin	...
	,,	1 : 2 : 3	,,	5-24	...	...
6.	,,	1 : 1 : 1.5	26-28°	6 weeks	Mono	69

TABLE VI

Products from 3 : 4-dihydroxybenzaldehyde.

	Products.	No.	M.P.	Cryst. shape.	Mol. formula.	Analysis (%). Found.	Calc.
1.	Ethyl (3 : 4-dihydroxybenzylidene)-*mono*-acetoacetate	I : R_1c	130°	Brown needles	$C_{13}H_{14}O_5$	C : 62.58 H : 5.40	62.4 5.6
2.	Ethyl (3 : 4-dihydroxybenzylidene)-*mono*-benzoylacetate	I : R_2c	172°	Brown cubes	$C_{18}H_{16}O_5$	C : 69.5 H : 5.6	69.23 5.12
3.	Ethyl (3 : 4-dihydroxybenzylidene)-*bis*-acetoacetate	IIc	163°	Green thin needles	$C_{19}H_{24}O_8$	C : 60.12 H : 6.99	60.0 6.7
4.	β-(3 : 4-dihydroxyphenyl)-glutaric acid	IVc	195° eff.	White needles	$C_{11}H_{12}O_6$	C : 55.22 H : 4.98	55.0 5.0
5.	1-Methyl-3-(3 : 4-dihydroxyphenyl)-2 : 4-dicarbethoxy-6-*cyclo*hexene-5-one	Vc	107°	Brown plates	$C_{19}H_{22}O_7$	C : 62.66 H : 5.96	62.98 6.07
6.	3-Methyl-4-(3 : 4-dihydroxybenzylidene)-*iso*xazolone-5	VI : R_1c	202°	Yellow cubes	$C_{11}H_{10}O_4N$	N : 6.12	6.3
7.	3-Phenyl-4-(3 : 4-dihydroxybenzylidene)-*iso*xazolone-5	VI : R_2c	204°	Pale yellow needles	$C_{16}H_{11}O_4N$	N : 5.24	4.99

From the data (Tables I-VI), it is generally seen that (*i*) the reactivity of mono hydroxybenzaldehydes is greater than that of the dihydroxybenzaldehydes, (*ii*) the reaction is slower but the yields are better with ethyl benzoylacetate than with ethyl acetoacetate and (*iii*) the reactivity of the bases is in the order: piperidine >lutidine >pyridine.

EXPERIMENTAL

The general procedure was, as before (Parts I and II, *loc. cit.*), to dissolve the aldehyde and the ester (1 : 1 or 1 : 2 moles) in a minimum quantity of cold or hot absolute alcohol, and to add to it an alcoholic solution of piperidine (0.1 mole., 3.8 by volume). The contents were kept at room temperature till complete solidification occurred. With pyridine or lutidine, the method was to mix the two reactants and the base in 1 : 1 : 6 or 3, or 1 : 2 : 6 molar proportions, and to heat them on a water-bath for 5 to 10 hours, or even longer, till a drop of the reaction mixture gave a precipitate or a turbidity with dilute HCl. In the case of 3 : 4-dihydroxybenzaldehyde, heating with tertiary bases gave a resinous mass ; these condensations were therefore carried out at room temperature without any solvent. Solidification took place in 3 to 6 weeks (Table V). After completion, the reaction product, if solid, was filtered and washed with dilute alcohol (40%). The filtrate usually provied more product on adding water. Where solidification did not occur, the liquid reaction mixtures were acidified with HCl (dil.) and the products were thus precipitated out, leaving the excess of base in solution. Recrystallisation in all cases was done from absolute alcohol or from glacial acetic acid, both furnishing pure products, but glacial acetic acid afforded colorless (white) crystals, while alcohol left a slightly yellow colour behind.

For the distinction between the mono-(I) and the *bis*-(II) esters, the general tests were as detailed below.

Baeyer's reagent (alkaline $KMnO_4$) was decolorised at once (within one second) in the case of the mono-ester, while decolorisation took place very slowly (from 30 to 100 seconds) in case of the *bis*-ester. The mono-ester also decolorised bromine water in cold, but the *bis*-ester did not. Tetranitromethane developed a very pale yellow colour with the saturated *bis*-esters and a very deep yellow colour with the unsaturated mono-esters. The benzoylacetic esters showed a deep red colour with cold H_2SO_4 (conc.) which on warming turned yellow, if *mono*, and brown, if *bis*. The melting points of the *bis*-esters were always higher than those of the mono-esters. Both the esters were soluble in alcohol, acetone and ether, and insoluble in benzene, chloroform and carbon tetrachloride ; but while the mono-ester was soluble in hot water and insoluble in cold water and in cold or hot glacial acetic acid, the *bis*-ester was insoluble in hot water and soluble in hot glacial acetic acid.

Hydrolysis.—α-Acetyl- or α-benzoyl-monohydroxycinnamic acids (III) were prepared from the mono-esters (I) by hydrolysis with a 5% solution of NaOH. Usually mixing 1 g. of the ester and 10 c.c. of 5% alkali and leaving overnight afforded on neutralisation the required acid. In some cases the ester had to be dissolved at start in warm alkali. All these acids decolorised Baeyer's reagent.

β-(Mono- or dihydroxyphenyl)-glutaric acids (IV) were obtained from the *bis*-esters (II) of the acetoacetic ester by alkaline hydrolysis. The ester and 40% KOH were mixed and were refluxed directly for 4 to 6 hours.

The three *cyclo*keto-di-esters (V) were also obtained from the *bis*-products (II) of acetoacetic ester. The *bis*-product (2.3 g.) was refluxed with a mixture of glacial acetic acid (4 c.c.), acetic anhydride (0.6 c.c.) and phosphoric acid (85%, 0.5 c.c.) on a low flame for 2 to 3 hours. The cooled contents were added to 50 c.c. of water and the oily product was extracted with ether. The ethereal solution was first neutralised with Na_2CO_3 and was washed successively with 5% NaOH, 5% acetic acid and water. The ether was evaporated and the residue was recrystallised from absolute alcohol.

The 3-methyl- or 3-phenyl-4-(mono or dihydroxy-benzylidene)-*iso*xazolones-5 (VI) were prepared from all the six mono-esters (I). The mono-ester and hydroxylamine hydrochloride (1 : 1 mole) were dissolved together in a little absolute alcohol, a few drops of NaOH (5%) were added and the mixture was refluxed on a water-bath for 1 hour. The crystals of (VI) separated out on cooling or on leaving overnight in ice.

The two *bis*-esters (II) from the two monohydroxybenzaldehydes gave red needles of the corresponding 2 : 4-dinitrophenylhydrazones in a few minutes on a water-bath.

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ANALYTICAL ASPECTS OF SOME ORGANIC COMPOUNDS. PART V. 2-HYDROXY-3-NAPHTHOIC ACIDS: DETERMINATION OF COBALT

By Sachindra Kumar Datta

Analytical properties of 2-hydroxy-3-naphthoic acid and its nitro, bromo, iodo, acetyl and nitroso derivatives have been studied. Thorium and zirconium form more or less quantitative precipitates with all these acids. The nitro derivative affords almost a quantitative precipitate with titanium as well. The nitroso derivative could be used for the determination of cobalt, palladium and uranium in addition to thorium. The gravimetric determination of cobalt and its separation from nickel and other elements with the nitroso derivative have been described.

The analytical uses of 1-hydroxy-2-naphthoic acid and its derivatives were previously studied (this *Journal*, 1956, **33**, 257, 394). In the present communication, 2-hydroxy-3-naphthoic acid and its bromo, iodo, nitro, acetyl and nitroso derivatives have been examined for their analytical properties. All these compounds produce quantitative precipitation of thorium and zirconium. The dinitro derivative may be used for the quantitative estimation of titanium. The nitroso compound forms red, red-brown and orange precipitates with cobalt, palladium and uranium respectively. These metals may be determined gravimetrically with this reagent. The preparation of the derivatives of 2-hydroxy-3-naphthoic acid and the use of 1-nitroso-2-hydroxy-3-naphthoic acid in the quantitative estimation of cobalt have also been described in this paper.

Experimental

Reagent grade (B.D.H.) 2-hydroxy-3-naphthoic acid was crystallised repeatedly from alcohol until its melting point rose to 222°. The derivatives of this acid were prepared from it by adopting the following methods.

4:6-*Dinitro-2-hydroxy-3-naphthoic Acid*.—Hydroxynaphthoic acid (18 g.) was taken in a large conical flask and to it was added about 25 c.c. of fuming nitric acid slowly with agitation of the flask and cooling under the tap after each addition. Vigorous reaction took place. After the reaction had subsided, about 500 c.c. of water was added to the mass and boiled for 10 minutes. The mixture was filtered after cooling, and washed with water. The reddish orange dinitro compound was crystallised from water, m. p. 138°. (Found: N, 10.23. Calc. for $C_{11}H_6O_7N_2$: N, 10.07 %).

1-*Bromo-2-hydroxy-3-naphthoic Acid*.—Hydroxynaphthoic acid (18 g.) was dissolved in 100 c.c. of absolute alcohol and cooled in ice. To this was added dropwise with stirring bromine (5 %, 8 g.) in glacial acetic acid solution, maintaining the temperature of the mixture below 10° during bromination. The mixture was then poured on a large volume of water when a pale yellow voluminous precipitate formed, which on stirring was converted into a gummy mass. The mass was extracted with ether and then dissolved in alcohol, after removing the ether. On pouring the alcoholic solution on cold water, a voluminous yellow precipitate was formed, m.p. 165°. (Found: Br, 29.04. Calc. for $C_{11}H_7O_3Br$: Br, 29.96 %).

1 : 6-*Di-iodo*-2-*hydroxy*-3-*naphthoic Acid*.—To a solution of hydroxynaphthoic acid (1 mole) in alcohol, cooled in ice, was slowly added a freshly prepared solution of ICl in glacial acetic acid (5%) with constant stirring. The mixture was kept in darkness for about 15 minutes and then it was poured on a large volume of water. The resulting voluminous yellow precipitate was filtered, washed with hot water and crystallised from alcohol (1 : 1), m.p. 215°. (Found : I, 57.2. Calc. for $C_{11}H_6O_3I_2$: I, 57.7%).

2-*Acetyl*-3-*naphthoic Acid*.—To hydroxynaphthoic acid (18 g.) in a dry conical flask were added 25 c.c. of acetic anhydride and then 3 drops of H_2SO_4 (conc.). The mixture was shaken for half-an-hour and then heated on a water-bath for 15 minutes until the solution became clear. It was cooled and cold water was added to the mass, filtered and washed with water. The white solid, thus obtained, was crystallised from alcohol, m.p. 185°.

1-*Nitroso*-2-*hydroxy*-3-*naphthoic Acid*.—A method similar to that for the synthesis of 1-nitroso-β-naphthol (Marvel and Patter, "Organic Synthesis", 1922, **2**, p. 61) was adopted for the preparation of this reagent with a little modification. Hydroxynaphthoic acid (36 g.) was dissolved in NaOH solution (10%, 10 g.) in water, with the aid of heat. It was cooled and diluted to 200 c.c. with water. The solution was then further cooled to 0° by a freezing mixture. $NaNO_2$ (18 g) in water (50 c. c.) was then added with vigorous stirring. To this mixture, now kept at 0° by adding crushed ice from time to time, was added dilute sulphuric acid very slowly with stirring, till the solution became acidic to Congo red. 1-Nitroso-2-hydroxy-3-naphthoic acid separated in the form of a brick-red precipitate. The stirring was continued for $\frac{1}{2}$ hour more. The product was filtered, washed with water and finally crystallised from alcohol, m.p. 190°. (Found : N, 6.11. Calc. for $C_{11}H_7O_4N$: N, 6.45%).

Possible Use in Qualitative and Quantitative Analysis

Stock molar solutions of Ag, Hg (ous and ic), Pb, Cu, Cd, Bi, Sb, Sn, Fe (ous and ic), Al, Cr, Mn, Zn, Co, Ni, Ca, Ba, Sr, Mg, Pd, Th, Zr, U, V, Th and Pt were prepared from their soluble salts. To 1 c.c. each of the salt solution were added 2 c.c. of the acetate buffer and 1% solution of the reagent in hot water or alcohol (1 : 1). For p_H higher than 7, ammoniacal solutions, where possible, were used. The colour change or precipitation was noted in each case. The washed precipitates were examined for the presence of the metal by decomposing them with concentrated mineral acids and applying standard tests. To examine the complete precipitation, the filtrate from the washed precipitate, obtained by the addition of the reagent in excess, was tested for the absence of the cation. The results of such tests with the reagents prepared are summarised below.

(1). 2-*Hydroxy*-3-*naphthoic acid* : Alcoholic solution produced blue and orange coloration with Fe^{III} and U at p_H 1.8 and higher. Th and Zr formed quantitative precipitation in presence of ammonium acetate at p_H 3.5. These salts are soluble in dilute acids, ammonium carbonate and in excess of ammonium acetate, but insoluble in alcohol. Precipitations of Hg^{I}, Pb and Ce^{IV} were not quantitative.

(2). 4:6-*Dinitro-2-hydroxy-3-naphthoic acid*: Hg^{I}, Pb and Ce^{IV} fromed yellow, yellowish white and deep yellow precipitate, respectively, at p_H 2.5 and even lower. Precipitation with Ce^{IV} was quantitative. Ti, Th and Zr also gave yellow quantitative precipitation at p_H 3. Mn and Al showed a slight turbidity at p_H 7.5 and 2.5 respectively. Fe^{III} produced a brownish red coloration at p_H 2, which deepened on boiling. Titanium salt was slightly soluble, while those of Ce^{IV}, Th and Zr were completely insoluble in hot water.

(3). 1-*Bromo-2-hydroxy-3-naphthoic acid*: Alcoholic solution produced bluish green and pale blue coloration with Fe^{II} and Fe^{III} respectively. Similar precipitates, as obtained with reagent No. 1, were also obtained with Hg^{I}, Pb and Ce^{IV} in this case. Precipitations, however, were incomplete. Thorium and zirconium formed colorless salts.

(4). 1:6-*Di-iodo-2-hydroxy-3-naphthoic acid*: Hg^{I}, Pb and Ce^{IV} produced incomplete precipitation. Yellow precipitates of Th and Zr were obtained with alcoholic solution. Such precipitation was quantitative.

(5). 2-*Acetyl-3-naphthoic acid*: This reagent gave no coloration with Fe (ous & ic) and U and produced almost quantitative precipitation with Th and Zr.

(6). 1-*Nitroso-2-hydroxy-3-naphthoic acid*: Aqueous solution of the reagent showed green coloration with copper in ammoniacal solution. Hg^{I} formed a deep orange precipitate, sparingly soluble the hot; Hg^{II} formed a precipitate in the cold, changing to brown on boiling. Pb formed a yellow precipitate, soluble in the hot. Fe^{II} gave a green precipitate, while Fe^{III}, a brown colour. Be showed a yellowish green coloration, and on standing, a slight green precipitate. Cerium^{IV} ammonium sulphate indicated a slight turbidity, while a deep orange precipitate appeared with ceric nitrate. Cobalt in acetic acid medium produced a red precipitate, while Th, Zr, Pd and U formed pale orange, orange, red-brown and orange precipitation respectively within a p_H range 2 to 5. Precipitation of Ce^{IV}, Co, Th, Zr, Pd and U appeared to be quantitative. These salts are soluble in high acid concentration and several of them are even soluble in some organic solvents.

Determination of Cobalt with 1-Nitroso-2-hydroxy-3-naphthoic Acid

Organic reagents for the determination of cobalt are many, of which mention may be made of anthranilic acid (Funk and Ditt, *Z. anal. Chem.*, 1933, **93**, 241), 8-hydroxyquinolipe (Fleck, *Analyst*, 1937, **62**, 378), phenylthiohydantoic acid (Willard and Hall, *J. Amer. Chem. Soc.*, 1922, **44**, 2119), pyridine (Spacu and Dick, *Z. anal. Chem.*, 1927, **71**, 97) and tetraphenylarsonium chloride (Pepkowitz and Marley, *Anal. Chem*, 1955, **27**, 1330).

Of the various derivatives of naphthol that have been used in the estimation of cobalt, α-nitroso-β-naphthol (Mayer and Feigl, *Z. anal. Chem.*, 1932, **90**, 15) has proved most effective. Other naphthol derivatives which are found to chelate with cobalt are: 2-nitroso-1-naphthol-4-sulphonic acid (Wise and Brandt, *Anal. Chem.*, 1954, **26**, 693)

nitroso-R-salt (McPherson and Stewart, *J. Biol. Chem.*, 1938, **32**, 763), 2 : 7-dinitroso-chromotropic acid (Teigmann. *J. Soc. Chem. Ind.*, 1943, **63**, 42), and 1-(2-pyridylazo)-2-naphthol (Cheng and Bray, *Anal. Chem.*, 1955, **27**, 782). The use of 1-nitroso-2-hydroxy-3-naphthoic acid, described in this paper, has been proved successful in the gravimetric estimation of cobalt and its separation from nickel and other foreign ions.

An 1% solution of 1-nitroso-2-hydroxy-3-naphthoic acid was prepared in hot water and filtered. A deep orange-coloured solution was obtained. A fresh solution was prepared daily.

The reagent (1 g.) was dissolved in 30 c.c. glacial acetic acid with the aid of heat ; the solution was then diluted to 100 c.c. with water. A greenish orange solution resulted, which was filtered and then used. A stock solution of cobalt was prepared from the reagent grade $CoCl_2,2H_2O$ and estimated by the standard method.

Cobalt Complex: *Method* I.—A solution of cobaltous chloride was diluted to 50 c. c. and was brought to boil ; to this solution was added dropwise with stirring an 1% solution of the reagent in hot water, when a reddish brown precipitate appeared which on boiling for 2 minutes coagulated and collected towards the centre of the beaker. The precipitate was allowed to stand for 2 hours and then filtered in a weighed sintered crucible, washed with hot aetic acid (1 : 2) and then with boiling water. The cobalt salt was then dried in an electric oven at 130° to a constant weight.

Method II.—In this method Co^{II} was converted to Co^{III} by following the procedure of Mayer and Feigl (*loc. cit.*). A known volume of the standard cobalt solution was taken in a 250 c.c. beaker and 1 c. c. of 30 volume H_2O_2 was added to it, followed by dilute NaOH till the solution became distinctly alkaline. A brisk effervescence of oxygen took place and the beaker was kept covered with a clock glass. When the reaction had subsided, the black cobaltic oxide was dissolved by adding about 15 c.c. of glacial acetic acid with the aid of heat. The solution was then diluted to 100 c. c. and was brought to boil. To this was now added the solution of the reagent in acetic acid till the precipitation was complete. A deep red precipitate formed which was digested on a water-bath for 20 minutes. The precipitate was allowed to stand for one hour and then filtered through a sintered crucible, washed and dried similarly as in method I.

Composition of the Cobalt Salt.—In order to find out the composition of the cobalt complex, a weighed quantity of the salt (containing a few mg. of Co), prepared under methods I and II, was separately ignited carefully in a platinum crucible in an oxidising atmosphere at 750°-850°, adding a few drops of HNO_3 towards the end. After cooling, the mass was weighed as cobalto-cobaltic oxide, Co_3O_4. Cobalt in the salt was also determined as $CoSO_4$ (Vogel, "Quantitative Analysis", 1953, p. 459). The results of analysis have been recorded in Table I. The salt obtained by method I gave a composition, as cobalt : reagent ratio = 3 : 1. This indicates that the complex may have a formula : $Co(C_{11}H_6O_4N)_3$. But the cobalt salt, obtained by method II seems to have the composition $Co(C_{11}H_6O_4N)_4$ or more probably $Co(C_{11}H_6O_4N)_2$, $(C_{11}H_7O_4N)_2$ as the latter formula is more definite. Determination of Co^{II} after its oxidation with H_2O_2 is preferable.

TABLE I

Analysis of cobalt complex.

Cobalt salt (dried at 130°).	Co found by Ignition.	Sulphate	Co. (calc from salt).
	Salt obtained by method I.		
0.0246 g.	0.0016 g.	0.0018 g.	0.0020 g.
0.0310	0.0020	0.0022	0.0026
0.0538	0.0049	0.0042	0.0045
	Salt obtained by method II.		
0.0291	0.0016	0.0017	0.0019
0.0386	0.0021	0.0029	0.0025
0.0602	0.0035	0.0036	0.0038

Optimum Conditions for the Determination of Cobalt

H-*ion Concentration*.—With a view to studying the p_H ranges over which cobalt could be completely precipitated with this reagent by method II, p_H of the solution was varied by adding acetate buffer solution or ammonium chloride and ammonia. The precipitation was carried out as before, the salt weighed and the amount of cobalt calculated on the assumption that 4 : 1 reagent-cobalt complex formed. The suitable p_H range, thus observed, was from 2 to 4.7. The results are shown in Table II.

TABLE II

Effect of p_H on the precipitation of cobalt.

Cobalt taken = 0.0032 g.

p_H	1.3	2.1	2.8	3.4	4.2	4.7	5.3
Co salt (g.)	0.0307	0.0528	0.0532	0.0529	0.0531	0.0525	0.0403
Co found (g.)	0.00195	0.00336	0.00338	0.00370	0.00338	0.00334	0.00256
Error (mg.)	−1.2	+0.2	+0.2	+0.2	+ 0.2	+ 0.1	− 0.6

Temperature of Drying.—It was found that the salt should be dried between temperatures 125° and 130° before weighing to get the results corresponding to the formula $(C_{11}H_6O_4N)_2$-Co, $(C_{11}H_7O_4N)_2$. The salt dried at various temperatures gave results shown in Table III. The composition of the salt becomes definite when it is dried at 130° or above.

TABLE III

Co taken.	Temp. of drying.	Co salt.	Co found (sulpate method).	Probable composition.
0.0064 g.	110°	0.1088 g.	0.0068 g.	$(C_{11}H_6O_4N)_4$-Co, H_2O
0.0064	115°	0 0976	0.0061	Do
0.0064	120°	0 1072	0.0067	Do
0.0064	125°	0.1075	0.0067	Do
0.0064	130°	0.1021	0.0065	$(C_{11}H_6O_4N)_2$ Co, $(C_{11}H_7O_4N)_2$
0.0064	140°	0.1036	0.0066	Do

Analytical Procedure.—A solution of cobalt containing about 5 mg. of cobalt, taken in a beaker, was diluted to about 30 c.c. and this was oxidised by adding a few drops of H_2O_2 (30 vol.). To this was added with stirring 0.1*N*-NaOH till the mixture became alkaline. The beaker was kept covered with a clock glass until the effervescence due to oxygen had ceased. The precipitated cobaltic oxide was dissolved with the aid of heat in the minimum quantity of acetic acid (1 : 1). The p_H of the solution was adjusted to 2.5 and then it was diluted to 100 c.c. This was boiled and to it was added an 1% solution of the reagent in dilute acetic acid. The precipitate was filtered, washed with dilute acetic acid and finally with hot water and dried in an electric oven at 130° to a constant weight. Co has been calculated from the formula: $(C_{11}H_5O_4N)_2$-Co, $(C_{11}H_6O_4N)_2$. The results have been compared with those obtained by estimating Co with anthranilic acid, and recorded in Table IV.

TABLE IV

	1-NO-2-OH-3-naphthoic acid.		Anthranilic acid.	
Co taken.	Wt of Co salt.	Co calc.	Wt. of Co salt	Co calc.
0.0072 g.	0.1086 g.	0.0069 g.	0.0410 g.	0.0073 g.
0.0064	0.1083	0.0069	0.0354	0.0065
0.0048	0.0816	0.0052	0.0281	0.0050
0.0032	0.0565	0.0036	0.0185	0.0033
0.0024	0.0424	0.0027	0.0124	0.0022

Precipitation Limit.—The reagent was proved to be highly sensitive for cobalt. Cobalt was precipitated even from solutions having concentration $1 : 10^6$, below which only red coloration was produced. The reagent may be used for the qualitative detection of cobalt even in presence of nickel.

Separation from Nickel.—To a solution of cobalt an aliquot quantity of a standard nickel solution was added. Cobalt was determined in the mixture by following the same procedure. The results recorded in Table V indicate that an excessive amount of nickel, if present in the mixture, interferes in the determination of cobalt.

TABLE V

Metals present.	Co salt.	Co found.	Metals present.	Co salt.	Co found.
Co : 0.0024	0.0345 g.	0.0021 g.	0.0048 g.	0.0836 g.	0.0053 g.
Ni : 0.0036	...	...	0.0198	...	...
Co : 0.0024	0.0449	0.0028	0.0048	0.0911	0.0058
Ni : 0.0054	...	...	0.0216	...	...
Co : 0.0024	0.0455	0.0029	0.0064	0.1193	0.0076
Ni : 0.0072	...	...	0.0288	...	...
Co : 0.0048	0.0832	0.0053	0.0064	0.0972	0.0081
Ni : 0.0180	...	...	0.0360	...	...

Effect of Diverse Ions.—A study was undertaken to determine which of the more common ions would interfere with the method. Cobalt was precipitated in presence of a large number of ions at p_H 2.5, by following the method I, as described before, and cobalt was determined as $CoSO_4$, as method II was time-consuming. Slight interference was noticed in case of Fe^{III} and aluminium. Mercury, lead, berillium, Fe^{II},

Ce^{IV}, thorium, zirconium, palladium and uranium, however, caused heavy interference as they were also co-precipitated more or less at the same p_H.

TABLE VI

Co taken=0.0064g.

Metal added.	Co found.	Metal added.	Co found.
Cu: 0.0312 g.	0.0068 g.	Ca: 0.0414 g.	0.0067 g.
Ba: 0.0205	0.0061	Sr: 0.0126	0.0067
Al: 0.0158	0.0069	Fe^{III}: 0.0139	0.0071
Cr: 0.0247	0.0062	Mn: 0.0103	0.0060
Mg: 0.0271	0.0063	Zn: 0.0312	0.0061
Cd: 0.0137	0.0068	Bi: 0.0233	0.0067

CONCULSION

Of the six organic compounds, the analytical properties of which have been described here, 1-nitroso-2-hydroxy-3-naphthoic acid has proved to be very useful in the gravimetric determination of cobalt. The composition of the cobalt complex of this acid is the same as that of the cobalt complex of α-nitroso β-naphthol. It is seen that the -COOH group present in the compound most probably does not take any part in linking cobalt. The advantage of this acid over α-nitroso-β-naphthol is that the former is easily soluble in water and forms more voluminous precipitate of cobalt than the latter. Most of the common ions do not interfere in the determination and cobalt may be separated from a considerable amount of nickel. The reagent may also find possible use in the colorimetric determination of cobalt.

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PREPARATION OF SULPHONES AND SULPHOXIDES OF SOME AROMATIC HYDROXYKETONES

By V. G. Kulkarni and G. V. Jadhav

Oxidation of 2 : 2′-dihydroxy-3 :3′-dimethyl-5 :5′-diacetyl-, 2 :2′-dihydroxy-3 :3′-diacetyl-5 :5′-dimethyl-, 3 : 3′-diacetyl-4 : 4′-dihydroxy - 6 : 6′ - dimethyl- and 3 :3′-diacetyl-4 :4′-dimethyl-6 :6′-dihydroxy-diphenyl sulphides with hydrogen peroxide in acetone solution furnished the corresponding sulphones.

Interaction of thionyl chloride and 3-methyl-4-hydroxy-, 2-hydroxy-5-methyl-, 2-hydroxy-4-methyl- and 2-methyl-4- hydroxy- acetophenones in presence of anhydrous aluminium chloride yielded the corresponding sulphoxides.

Among the various oxidising agents known to oxidise sulphides to sulphones, hydrogen peroxide is found to be the best, as it does not attack, in presence of a solvent, groups other than sulphide ; further, the isolation of the product is also easy. In the present work, oxidation was therefore carried out by means of hydrogen peroxide in presence of acetone. The oxidation products are assigned the constitution of sulphones, as they differ from the substances obtained by the action of thionyl chloride on aromatic hydroxyketones in presence of anhydrous aluminium chloride, when sulphoxides are obtained. It has been proved by Smiles and his co-workers that interaction of thionyl chloride and phenol and *p*-cresol in presence of anhydrous aluminium chloride furnishes sulphoxides (*J. Chem. Soc.*, 1907, **91**, 1118 ; 1910, **97**, 2249). Hence, the products obtained in thionyl chloride reaction have been assigned the sulphoxide constitution.

Experimental

The sulphide (1 g.) was dissolved in acetone (30 c.c.) and hydrogen peroxide (20 c. c., 100 vols.) was added to it. The mixture was well shaken, taking care to see that the sulphide remained in solution (more acetone being added, if necessary). The mixture was left overnight at room temperature. Usually the oxidation product separated in a crystalline form. It was filtered and washed with acetone yield 0.8 g. (approx.) in all cases. The results are described in Table I.

Table I

Sulphones ($C_{18}H_{18}O_6S$) *obtained from corresponding sulphides* ($C_{18}H_{18}O_4S$) *through oxidation.*

No.	Diphenyl sulphides.	M.P. of sulphones.	% Sulphur (found) *
1.	2 : 2′-Dihydroxy-3 :3′-dimethyl-5 :5′-diacetyl-	212-13°	8.92
2.	2 :2′-Dihydroxy-3 :3′-diacetyl-5 :5′-dimethyl-	222-23°	8.68
3.	3 :3′-Diacetyl-4 :4′-dihydroxy-6 :6′-dimethyl-	260-61°	8.96
4.	3 :3′-Diacetyl-4 :4′-dimethyl-6 :6′-dihydroxy-	159-60°	8.52

* $C_{18}H_{18}O_6S$ requires S, 8.84%.

Anhydrous aluminium chloride (4 g.) was dissolved in dry nitrobenzene (30 c.c.) and the requisite ketone (5 g.) was added to it. The mixture was allowed to cool to room temperature and then thionyl chloride (2.5 c.c.) was added and the whole mixture was allowed to stand for 24 hours. Usually the reaction mixture changed colour. The mixture was then poured into hydrochloric acid and nitrobenzene was removed. The residue was crystallised from a suitable solvent. With H_2SO_4 (conc.) sulphoxides (1) and (4) developed dark violet coloration, (2) gave red coloration and (3) gave a dark green coloration. These colours disappeared on addition of phenol. The results are described in Table II.

TABLE II

No.	Acetophenones.	Corresponding diphenyl sulphoxide.	Cryst. from.	M.P.	Yield.	Mol. formula	Found.
1.	3-Methyl-4-hydroxy-	2 :2′-Dihydroxy-3 :3′-dimethyl-5 :5′-diacetyl-	Benzene	168-69°	2 g.	$C_{18}H_{16}O_5S$	C ; 62.23; H, 5.28; S, 9.35.
2.	2-Hydroxy-5-methyl-	2 : 2′-Dihydroxy-3 :3′-diacetyl-5 :5′-dimethyl-	Acetic acid	260-61° (decomp.)	2	$C_{18}H_{16}O_5S$	C, 62.08; H, 5.17; S, 8.93.
3.	2-Hydroxy-4-methyl-	3 :3′-Diacetyl-4 : 4′-dihydroxy-6 :6′-dimethyl-	EtOH	120° (decomp.)	1	$C_{18}H_{16}O_5S$	C, 62.14; H, 5.01; S, 9.14.
4	4-Hydroxy-2-methyl*-	3 :3′-Diacetyl-4 :4′-dimethyl-5 :5′-dihydroxy- or 3 :3′-Diacetyl-2 :2′-dimethyl-6 :6′-dihydroxy-	$CHCl_3$	228-29°	1	$C_{18}H_{16}O_5S$	C, 62.07; H, 5.3; S, 9.15.

$C_{18}H_{16}O_5S$ requires C, 62.43; H, 5.2; S, 9.24%.

*Reaction mixture was kept at 0° instead at room temperature.

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SHORT NOTES

PISUM SATIVUM (LINN)

By Narayan Chandra Ganguly and Bidyut Kamal Bhattacharyya

Sanyal (*Calcutta Med. J.*, 1952, **49**, 343) reported the sterility effect of the oil of *Pisum sativum* Linn and isolated *m*-xylohydroquinone from the said oil. The author claims that the aforementioned compound is responsible for the sterility effect. In view of this important observation, an investigation on the non-saponifiable constituents of the oil is reported herein.

The oil was saponified with methanolic potassium hydroxide and the neutral material was chromatographed on alumina to furnish an oily and a waxy hydrocarbons of unknown constitution together with β-amyrin and β-sitosterol.

* *β-Amyrin and β-Sitosterol.*—Powdered seeds of *Pisum sativum* (4174 g.) were extracted with hot petroleum ether (b. p. 60°-80°) until the extract was colorless. After removal of the solvent the red oily residue (64 g.) was heated to reflux for 8 hours with potassium hydroxide (40 g.) in water (40 c.c.), methanol (300 c.c.) and benzene (300 c.c.). The mixture was diluted with water (1000 c.c.) and then extracted with ether in a continuous extraction apparatus. The ethereal solution after washing with water was dried over anhydrous sodium sulphate. The residue (23 g.), obtained after evaporation of the ether, was chromatographed on alumina (420 g.). The oily material (1.9 g.), eluted with petroleum ether (b. p. 60°-80°), was evaporatively distilled to yield (*i*) an oil, b.p. 80°/0.15 mm, η_D^{31} 1.4890 (Found : C, 87.10 ; H, 12.68%); (*ii*) a semi-solid material, b.p. 140-50°/0.1 mm (Found : C, 86.56; H, 13.76%). The material (600 mg.) eluted with benzene-petroleum ether (1 : 9 and 1 : 4) was rechromatographed on alumina to furnish a crystalline substance, m. p. 190-92° (80 mg.) which was crystallised six times from methanol to yield β-amyrin, m.p. 200-201° ; $[\alpha]_D$ +96° ± 2°. (Found : C, 84.62 ; H, 11.81. Calc. for $C_{30}H_{50}O$: C, 84.43 ; H, 11.80%). Ames, Halsall and Jones (*J. Chem. Soc* , 1951, 450) record m.p. 197-99° ; $[\alpha]_D$ +91°.

The *acetate of* β-amyrin was prepared with acetic anhydride and pyridine at room temperature and then chromatographed to afford a pure material, m.p. 234-35° after crystallisation from a mixture of benzene and alcohol. (Found : C, 82.20 ; H, 11.08. Calc. for $C_{32}H_{52}O_2$: C, 81.98 ; H, 11.19%).

The solid material together with the oil (3 g.) eluted with benzene-petroleum ether (1 : 1) was rechromatographed to afford, after crystallisation from alcohol, β-sitosterol, m.p. 136-37°, $[\alpha]_D$ -34° ± 1°. (Found : C, 84.02 ; H, 12.02. Calc. for $C_{29}H_{50}O$: C, 83.98; H, 10.49%). The mixed m. p. with an authentic sample (Chatterjee and Bhattacharyya, this *Journal*, 1955, **32**, 485) remained undepressed.

The authors' thanks are due to Mrs. C. Dutta for microanalysis.

The m. p.'s are uncorrected.

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DETERMINATION OF WATER IN ACETIC ACID WITH ACETIC ANHYDRIDE AND ANILINE

By Mihir Nath Das

The simplest method for the determination of water in organic compounds is based on the reaction of water with acetic anhydride or acetyl chloride, followed by titration with alkali (Smith and Bryant, *J. Amer. Chem. Soc.*, 1935, **57**, 841 ; Toennies and Elliott, *ibid.*, p. 2136). Other similar reagents that have been used for the same purpose include benzoic anhydride (Ross, *J. Soc. Chem. Ind.*, 1932, **51**, 121T), aluminium chloride (Fischbeck and Eckert, *Z. anal. Chem.*, 1938, **112**, 305), α-naphthyldichlorophosphine oxide (Lindner, *ibid* , 1925, **66**, 305), α-naphthoxydichlorophosphine (Bell, *J. Chem. Soc.*, 1932, 2903), cinnamoyl chloride (Van Nieuwenberg, *Mikrochim. Acta*, 1937, **1**, 71), etc. These acidimetric methods cannot, however, be used for the determination of small amounts of water in acetic acid or other acids. The Fischer titration (*Angew. Chem.*, 1935, **48**, 394) has recently found wide acceptance for determination of water in various compounds, and numerous improvements in the technique have been devised to suit specific requirements (Mitchell, Jr. and Smith, "Aquametry", Interscience, New York, 1949). The Fischer method has been used with success to determine small quantities of water in various organic and inorganic acids. But the cost and special techniques involved tend to restrict its use only to cases where determination of water is a matter of routine procedure.

The method described herein is based on the acid-catalysed reaction between water and a known amount of acetic anhydride, dissolved in glacial acetic acid, and estimation of the excess anhydride left unchanged. So, the problem ultimately reduces to the determination of acetic anhydride in acetic acid.

Toennies and Elliott's polarimetric method (*J. Amer. Chem. Soc.*, 1937, **59**, 902) for determination of acetic anhydride in glacial acetic acid depends on the measurement of the decrease in optical activity as a result of the reaction between camphoric acid and acetic anhydride, producing camphoric anhydride, the reaction being catalysed by small concentrations of strong acids. They have used this method for determination of water in acetic acid. Siggia and Hanna (*Anal. Chem.*, 1951, **23**, 1717) have determined several acid anhydrides in presence of carboxylic acids by allowing the anhydride to react with a known amount of aniline, and estimating the excess aniline by potentiometric titration in ethyleneglycol—*iso*propyl alcohol mixture. Benson and Kitchen (*Canadian J. Res.*, 1949, **27**, 266) have determined acetic anhydride in acetic acid with aniline by estimating the excess aniline colorimetrically with furfuraldehyde. Very recently (Greathouse *et al.*, *Anal. Chem.*, 1956, **28**, 357) the acid-catalysed reaction between water and acetic anhydride has been utilised for determination of either water or acetic anhydride in acetic acid by thermometric titration. According to the present method, the excess aniline is titrated directly with perchloric acid in

glacial acetic acid medium, using methyl violet as indicator. The acetanilide, formed by the reaction between acetic anhydride and aniline, is too weak a base even in glacial acetic acid medium, and does not interfere with the titration of free aniline.

Acetic anhydride solution (0.1-0.2*M*) in acetic acid containing 0.001*N*-$HClO_4$ was used. The solution was standardised with aniline as described below. The strength of the solution changed rather rapidly and was checked before use.

0.1*N*-Perchloric acid solution in glacial acetic acid, standardised with potassium hydrogen phthalate, using methyl violet or crystal violet as indicator (Seaman and Allen, *Anal. Chem.*, 1951, **23**, 591), was employed. 72% Perchloric acid may be used for preparation of the standard solution; the water introduced with the acid does not interfere.

Aniline was freshly distilled over caustic soda. A standard solution (0.1-0.2 *M*) of aniline in anhydrous acetic acid can be prepared as follows. To remove any moisture that may be present in "glacial" acetic acid, acetic anhydride is added (10 c.c. per litre of acid or more, if necessary) and allowed to stand overnight. Sufficient aniline is then added so that the final concentration of free aniline is 0.1-0.2 *M*, a part of the aniline being converted into acetanilide by reaction with free acetic anhydride. The solution was kept in a coloured glass-stoppered bottle and standardised by titration with 0.1 *N*-$HClO_4$ in acetic acid. The solution, so prepared and preserved, has been found to remain colorless and maintain constant strength for several days.

Glacial acetic acid used was distilled over anhydrous calcium sulphate. No special purification for removing traces of water is necessary. The solvent must be neutral to methyl violet (0.2% solution in glacial acetic acid).

Procedure: *Standardisation of acetic anhydride solution in acetic acid.*—A measured volume of the solution containing 2-3 millimoles of anhydride was treated with 3-4 millimoles of aniline in a glass-stoppered bottle or conical flask. After 5 minutes, the free aniline was titrated with 0.1 *N*-$HClO_4$ in glacial acetic acid using methyl violet as indicator. The first disappearance of violet tinge of the indicator was taken as the end-point.

Instead of using a standard solution of aniline, the base may be directly weighed out into the acetic anhydride, but the purity of aniline must be checked by titration with $HClO_4$ in acetic acid. The precision of the method was tested by determining acetic anhydride in acetic acid in replicates, using the same solution. The reproducibility data are presented in Table I.

TABLE I

Number ...	1	2	3	4	5
Molar conc. of anhydride found	0.1068	0.1073	0.1070	0.1071	0.1074

Average 0.1071 ± 0.0003

Determination of water in acetic acid.—Different amounts of water were directly weighed out into a known volume of the standard solution of acetic anhydride in a glass-stoppered bottle or conical flask. The hydrolysis of acetic anhydride was strongly catalysed by $HClO_4$ (0.001 *N*) present in the solution, and the reaction was complete in less than 10 minutes. The excess of acetic anhydride was then estimated with aniline as described above. Results are shown in Table II.

TABLE II

Water taken.	Conc. of water in reaction mixture.	Water found.	% Error.
0 2267 g.	0.45 %	0.2259 g.	−0.35
0.1427	0 29	0.1416	−0 77
0.0918	0.46	0.0910	−0.87
0.0825	0.41	0.0827	+0 25
0.0480	0.16	0.0485	+1.04
0.0468	0.09	0 0470	+0.43

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SPECTROPHOTOMETRIC DETERMINATION OF THE DISSOCIATION CONSTANT OF HYDROXYLAMINE

BY S. S. MUHAMMAD AND T. NAVANEETH RAO

The preseLt work was undertaken in order to check independently the va'ue of the dissociation constant of hydroxylamine, obtained conductometrically in this laboratory (this *Journal*, 1957, **34**, 101). Experiments showed that in the case of hydroxylamine, the method of Stenström and Goldsmith (*J. Phys. Chem.*, 1926, **30**, 1683) was the most suitable.

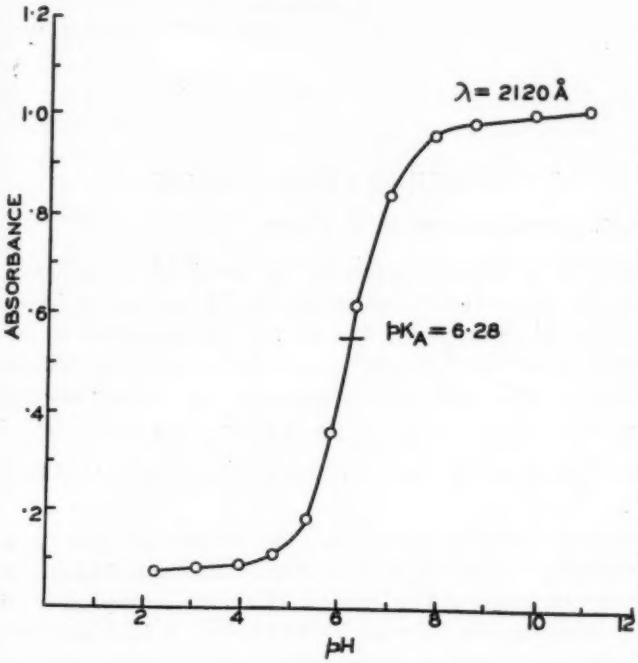
Hydroxylamine is known to be highly diactinic in the aqueous solution (Hartley and Dobbie, *J. Chem. Soc.*, 1900, **77**, 318) as in the gas phase (Smith and Leighton, *J. Amer. Chem. Soc.*, 1944, **66**, 172) ; it exhibits continuous absorption in the region 2015 to 2350Å or further, depending on the length of the optical path and the concentration or pressure of hydroxylamine. This shows that unlike aniline (Flexser *et al.*, *ibid.*, 1935, **57**, 2103) and pyridine (Andon *et al.*, *Trans. Faraday Soc.*, 1954, **50**, 910) here concentrated solutions and longer optical paths have to be used.

The apparatus consisted of a Unicam quartz spectrophotometer (model Sp. 500), a hydrogen lamp combined with a stabilised power pack and quartz cells of 4 cm optical path. A series of phosphate buffers (p_H 2 to 11) made from $M/10$-H_3PO_4 and $M/10$-KOH were prepared and their p_H was determined on a Beckman model-G p_H-meter, previously standardised against standard buffers.

Pure hydroxylamine was prepared by the method of Hurd and Brownstein (*J. Amer. Chem. Soc.*, 1925, **47**, 67). It was dissolved in water to form a strong solution, the strength of which was determined by the bromate method. It was then diluted to $\sim M/2$; 1 c.c. of this was diluted to 25 c.c. by adding the required buffer. Tests showed that this solution had the same p_H as the original buffer. The blank contained the appropriate buffer to which 1 c.c. of distilled water was added. The absorption measurements were

taken in the range 2100 to 2400 Å at the room temperature of 30° which varied within ±0.5° during the experiments. The data so obtained may be used to construct spectrophotometric titration curves at desired wave-lengths. A graph of absorbance against p_H at 2120 Å is shown in Fig. 1.

FIG 1



To find the mid-point of the break in the curve, a graphical analysis as, suggested by Slabaugh and Cates (*Anal. Chem.*, 1055, **27**, 151), was carried out by bisecting the distance between the linear portions of the curve prior to and following the inflexion. This gave a pK value of 6.28 at 2120 Å. Similar treatments of the data at 2140, 2160 and 2180Å yield the values 6.27, 6.25 and 6.25 respectively. The mean 6.263 is the apparent pK value. The apparent dissociation constant is related with the thermodynamic dissociation constant by the relation :

$$pK_A = pK + \log_{10} \gamma BH^+$$

where pK_A refers to thermodynamic equilibrium :

$$[NH_3OH]^+ \rightleftharpoons NH_2OH + H^+$$

and γBH^+ is the activity coefficient of the base cation $(NH_3OH)^+$. The latter can be calculated from the approximate Debye-Hückel equation :

$$\log_{10} \gamma BH^+ = \frac{-0.5\, z^2 \sqrt{\mu}}{1 + \sqrt{\mu}}$$

where z denotes valency of the base cation, equal to 1 for hydroxylamine, and μ = ionic strength of the medium. At p_H 6.25 the phosphoric acid —KOH mixture corresponds to an ionic strength $\sqrt{\mu}=0.264$ and $\log_{10} \gamma BH^+ = -0.105$, which makes $pK_A = 6.158$. But the basic dissociation constant pK_B for the equilibrium :

$$NH_2OH + H_2O \rightleftharpoons (NH_3OH)^+ + OH^-$$

can be obtained from the relation

$$pK_B = pK_W - pK_A.$$

According to Harned and Owen ("Physical Chemistry of Electrolytic Solutions", p. 485, Reinhold Pub. 2nd edition) pK_w at 30° is 13.833. Therefore pK_b at 30° = 7.675 and $K_b = 2.113 \times 10^{-8}$. This compares closely with the value 2.202×10^{-8} for the dissociation constant derived from conductometric determination of the hydrolysis of hydroxylamine hydrochloride, reported previously (*loc. cit.*).

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REDUCTION OF DICHROMATE BY FERROCYANIDE

BY K. CHATTERJEE AND B. P. GYANI

Much interesting information is available regarding the oxidising properties of $K_2Cr_2O_7$. Its reduction by iodide ions was studied potentiometrically in detail by Gyani and Prasad (this *Journal*, 1954, **31**, 561; 1955, **32**, 313). The reduction of the dichromate ion by the ferrocyanide ion was first studied potentiometrically by Someya (*Z. anorg. allgem. Chem.*, 1926, **159**, 158), who found that the redox reaction

$$HCrO_4^- + 3Fe(CN)_6^{4-} + 7H^+ = Cr^{3+} + 3Fe(CN)_6^{3-} + 4H_2O$$

could be followed potentiometrically at 40°-65° in 5 to 10 c.c. HCl per 60 c.c. of the total volume.

Someya's work refers to strictly specified conditions. The present work was taken up to carry out a fuller investigation of this reaction in different concentrations of two different acids at ordinary temperatures. The use of potassium ferrocyanide for standardisation of potassium permanganate solution is well known. It is of interest to know whether the ferrocyanide itself could be standardised with a readily available substance like $K_2Cr_2O_7$.

A. R. grade $K_2Cr_2O_7$ was taken and prepared for use as usual. Finely powdered crystals of A.R. $K_4Fe(CN)_6, 3H_2O$ were dried to a constant weight over a saturated solution of NaBr (Vogel, "Quantitative Analysis", London, 1951, p. 271). Titrations were carried out in a three-necked Woulff's bottle in which 100 c.c. of 0.005 *M* solutions of $K_2Cr_2O_7$ in different concentrations of sulphuric acid (12*N*, 8*N*, 6*N*, 4*N*, 2*N*, *N*, *N*/2, *N*/4, and *N*/10) and HCl (2*N*, *N*, *N*/2, and *N*/4) were taken. The titrations were carried out in the usual manner, using a bright platinum foil electrode at 28° ± 1° for H_2SO_4 mixtures and at 34° ± 1° for HCl mixtures.

The inflexions are quite steep in each case. When sulphuric acid concentrations lie between 6*N* and 1*N* or when HCl concentrations lie between *N*/2 and *N*/4, the inflexions correspond to 6 moles $K_4Fe(CN)_6$ per mole dichromate and the following mechanism is indicated:

$$Cr_2O_7^{2-} + 14H^+ + 6Fe(CN)_6^{4-} = 2Cr^{3+} + 7H_2O + 6Fe(CN)_6^{3-}.$$

Steady potentials are obtained in 15 to 20 minutes of each addition of the titrant and this period is somewhat longer when the acid concentrations are lower. It appears therefore

that Someya's work cannot only be extended to acids other than HCl but excellent agreement with theoretical requirements may also be obtained at ordinary temperatures under a wide range of acid concentrations.

When sulphuric acid concentration is greater than 6*N* or the HCl concentration is greater than normal, about half a mole less ferrocyanide is required. On the other hand, when sulphuric acid concentration is less than normal, a slight excess over 6 moles ferrocyanide is required. The inflexions are somewhat less steep at lower acid concentrations.

The colour changes of the reaction mixture are very interesting. The initial orange-yellow of the dichromate gradually darkens into a rich golden yellow with a greenish tinge as the ferrocyanide solution is being added. The colour turns a brilliant emerald-green when the point of inflexion is passed. The green colour sometimes develops only on keeping, often when an excess of ferrocyanide has been added.

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Free Chlorine (Cl) :	—	—	0.0002 %
Nitrate (NO_3) :	0.00002 %	—	—
Iodate (IO_3) :	—	0.0005 %	—
Sulphate (SO_4) :	—	0.0003 %	0.0003 %
Heavy Metals (Pb) :	0.0002 %	0.0002 %	0.0002 %
Iron (Fe) :	0.0001 %	0.0001 %	0.0001 %
Arsenic (As_2O_3) :	0.00001 %	0.05 part per million	0.04 part per million
Ammonia (NH_3) :	0.0005 %	—	—
Oxygen Absorbed (O) :	1.0001 %	—	—

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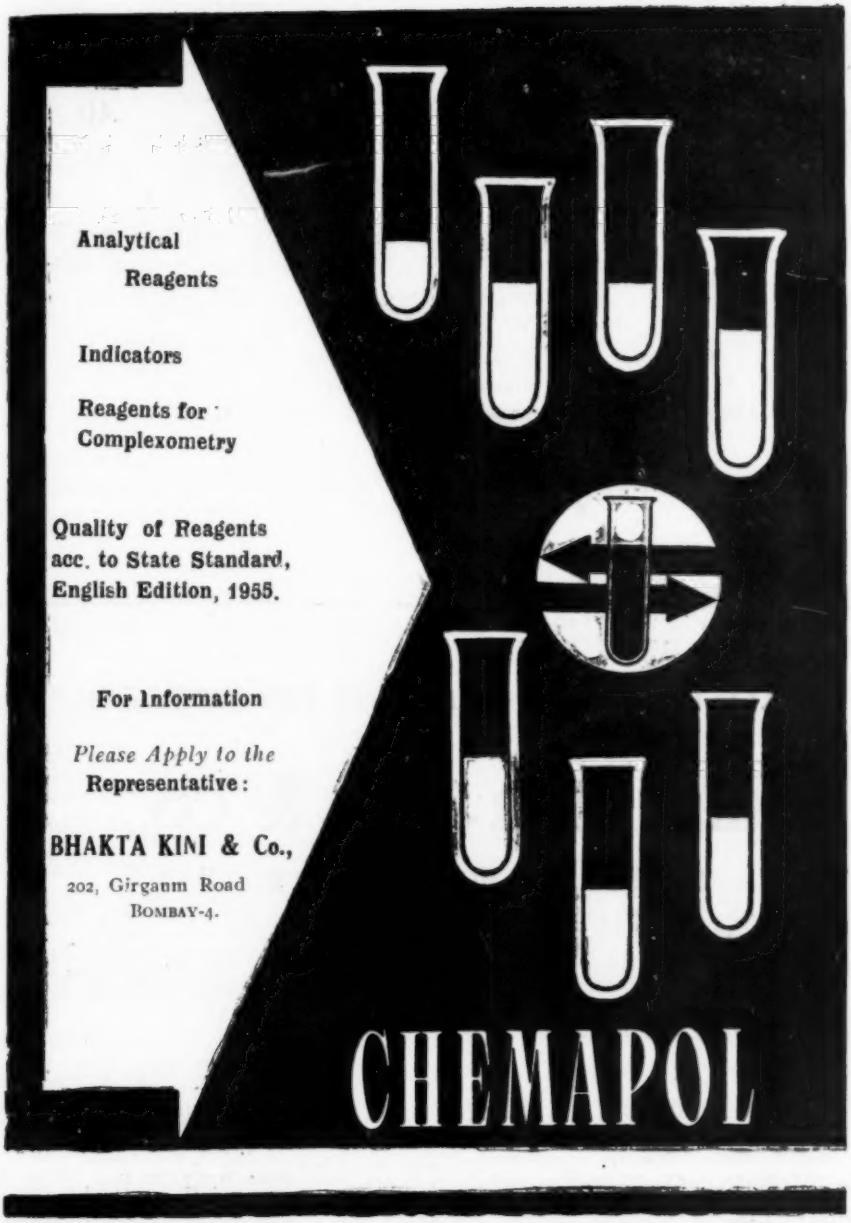

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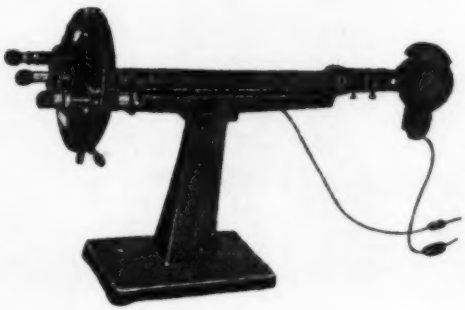

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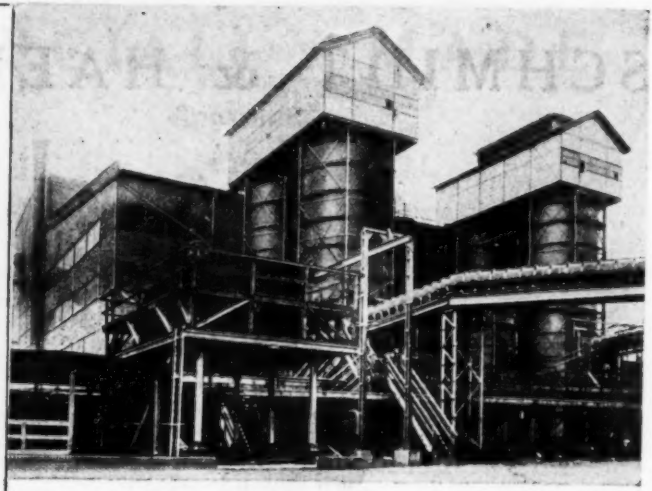

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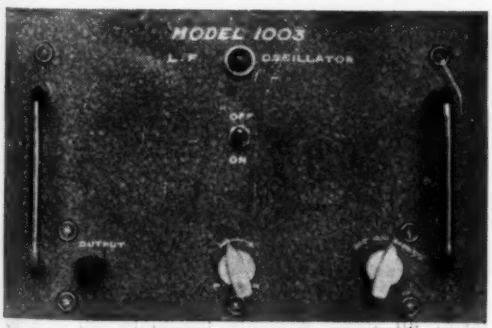

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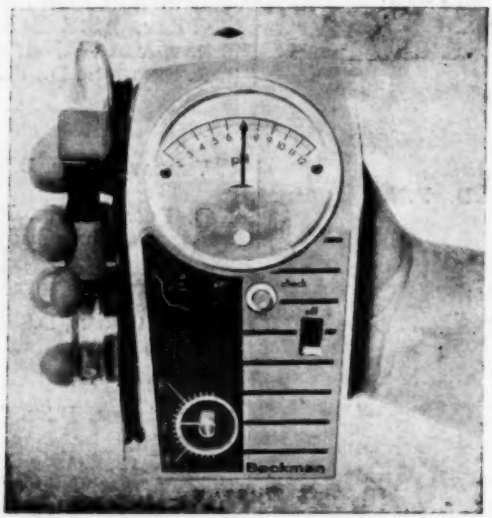

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